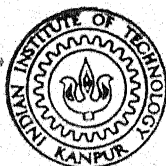


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DENSITY OF LIQUID HALOMETHANES

By

P. R. Patnaik, P. P. Mishra and A. P. Kudchadker



Kanpur Critical Data Center

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DENSITIES OF LIQUID HALOMETHANES

Prepared by the Research Staff of the NBS-OSRD Research Project

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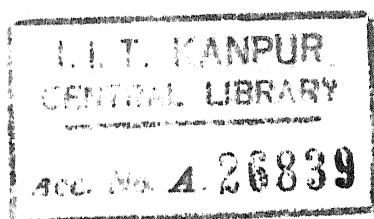
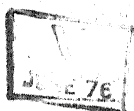
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TABLE OF CONTENTS

| | | | Page |
|------|-------------------------------------|-----|------|
| I. | INTRODUCTION | ... | 1 |
| II. | EVALUATION AND SELECTION PROCEEDURE | ... | 5 |
| III. | DETAILED DISCUSSION OF COMPOUNDS | ... | 11 |
| IV. | BIBLIOGRAPHY | ... | 48 |

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DENSITIES OF LIQUID HALOMETHANES

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ABSTRACT

The available density data for the liquid in air and the saturated liquid of the halogenated methanes have been critically reviewed. Of the sixty-nine halogenated methanes studied, densities for thirty-eight compounds have been reported independently by different investigators. Even among these, reliable data are available for only seventeen compounds. Selected data for these, and three other compounds have been correlated through relatively simple equations. The selection of "good" data was arrived at by carefully evaluating each set of data for its accuracy, method of experimentation, sample purity, etc. The selection procedure is discussed. The uncertainty in the selected value is reported. In certain cases, where no such information was available, we have had to rely entirely on the past reputation of the author(s). For interpolation and limited extrapolation, the quadratic and cubic equations in the absolute temperature have been used, except for the Martin equation for those compounds for which data up to the critical point were available. Within limitations of experimental errors, the simple

(ii)

temperature functions used relate the liquid and the saturated liquid densities very well over the available temperature ranges. Besides tabulating the results of the regressions, deviation plots have also been provided so as to furnish an overall pictorial representation of the "goodness of fit" in each case. The selected equations have been used to compute densities at intervals of 5°C. Where possible, calculated densities at 20°C and 25°C have been compared with selected values reported by the Thermodynamics Research Center. Of the twenty-five sets of regressions, the quadratic model was adequate in eleven cases. The Martin equation was selected in nine cases, mostly the mixed halomethanes.

Key words: Density; empirical correlation; liquid halomethanes; "good" data; regression equations - polynomial, Martin; selection.

INTRODUCTION

The densities of liquid halomethanes have been experimentally determined as early as 1893 by Ramsay and Shields, who reported density data for carbon tetrachloride in the saturated region from 20° to 250°C. From then to the present day, over eight decades, several authors have presented density measurements on a number of halomethanes. Many authors have measured densities at selected temperatures, usually around room temperature, primarily in the process of synthesizing and identifying the compound, while others have carried out accurate density versus temperature measurements on very pure samples in order to provide reliable data for process design calculations and for some theoretical studies. Among the earlier workers involved in carrying out accurate density measurements, Timmermans and his coworkers, in the late 1920's and early 1930's, have published reliable data for a number of these compounds. The data are however reported over a limited temperature range. The subsequent quarter century has been a rather lean period. Only as late as 1960 did good experimental values again begin to appear in the literature. While individual workers have been given due credit in the detailed discussion of compounds, one may specifically cite Morgan and Lowry, Dreisbach and Martin, Benning and McHarness, and Campbell and Chatterjee for their painstaking work. However, not even all of these have always

furnished "complete" experimental details such as sample purity, method of determination, accuracy of measurements, etc. This has considerably complicated proper selection both for recommendation of "good" data and for regression purposes. In general, it is only recently that authors report pertinent information necessary for a critical evaluation of their data, thanks to the publication policies of many journals.

Timmermans, Thermodynamics Research Center Data Project (T.R.C.), and American Society of Heating, Refrigerating, and Air Conditioning Engineers (ASHRAE) report critically selected data for quite a few halomethanes. In many cases our initial selections have been checked and cross-checked against the "selected" values by the above publications, especially by T.R.C.

Literature data are available for the liquid in air as well as for the saturated liquid region, both of which are compiled in the present work. A survey of sixty-nine halogenated methanes shows that density data are available for just thirty-nine compounds for the liquid in air and for the saturated liquid region. Out of these thirty-nine compounds, reliable experimental data up to the critical point are available for nine and up to the normal boiling point for ten halomethanes, mostly the fluoro- and chloro-compounds. Inadequate data are available for nineteen compounds, making selection difficult in these cases. It is surprising that even for a simple physical property like

density, accurate data are so meagre. The problems in general are probably the low temperatures involved, synthesis of mixed compounds, purification of the samples, decomposition at higher temperatures, etc. Table I analyzes available data and recommends future experimentation for several compounds due to the scarcity of "good" data. Systematic and intensive activity in these cases is desired.

The data reported in this investigation cover the period 1893 to June 1971, and were obtained in a large majority of the cases, from the original literature. Only in the case of obscure and inaccessible publications was it necessary to depend wholly on the Chemical Abstracts. For each compound data from each author were arranged in chronological order with increasing temperatures to study the trend in the values and to facilitate selection.

It was observed during the compilations that the temperature scales used by different investigators were not quite identical, because of periodic revision in the definitions of the fixed points and the units of measurement. For all our reported data we have strictly adhered to the International Practical Temperature Scale of 1968 (IPTS-1968), which differs somewhat from the earlier IPTS-1948. Principally, the defining point was changed from the freezing point of water to the triple point of water because the latter is more reproducible and stable. As a result, the following relations

hold:

$$T_{\text{triple point}} - T_{\text{ice point}} = (0.0100 \pm 0.0001) \text{ K}$$

$$t_{\text{triple point}} - t_{\text{ice point}} = (0.0100 \pm 0.0001)^{\circ}\text{C}$$

$$T_{\text{triple point}} = 273.16 \text{ K (exactly), by definition}$$

$$T_{\text{ice point}} = (273.15 \pm 0.0001) \text{ K}$$

$$t_{\text{triple point}} = 0.01^{\circ}\text{C (exactly)}$$

$$t_{\text{ice point}} = (0.0000 \pm 0.0001)^{\circ}\text{C}$$

The IPTS-1968 is valid upto temperatures as low as 90.188°K (-182.962°C) and therefore adequately covers the available density data. Density values reported on the basis of IPTS-1948 and other temperature scales have accordingly been updated to conform to the IPTS-1968 scale (139). Further, density values reported in other units have been converted to c.g.s. units, so that recorded densities are in g cm^{-3} , and all temperatures in degrees Celsius. The conversion factors used are taken from the International Union of Pure and Applied Chemistry (148).

$$1 \text{ lb} = 453.59237 \text{ g}$$

$$1 \text{ new ml} = 1 \text{ cm}^3 \text{ (exactly)}$$

$$1 \text{ in.} = 2.54 \text{ cr.}$$

$$1 \text{ g cm}^{-3} = 62.42795 \text{ lb ft}^{-3}$$

EVALUATION AND SELECTION PROCEDURE

For very few compounds was adequate accessory information available to facilitate assessment and data selection. Table I also represents the literature references for each halomethane. Those references from which data were selected for final analysis are underlined in Table I.

In the analysis, the work of each investigator was carefully scrutinized to ascertain the precision and accuracy of the actual measurements of densities and temperatures. The following points were considered in analyzing and evaluating the data.

- (i) Source, method of purification, and the purity of the sample.
- (ii) Method of measurement and calibration of the measuring instruments.
- (iii) Accuracy of parameter measurements, i.e. temperature, weight, liquid level, calibrating fluid density, etc.
- (iv) Computed accuracy in the final density value.
- (v) Reproducibility of results.
- (vi) Purpose of measurement.
- (vii) Number and closeness of data points.
- (viii) Range of investigated temperatures.
- (ix) Reputation of the authors.

A general evaluation methodology for the method of purification is not possible since the merit of a purification process is a function of the particular substance and the nature of impurities present. In some cases however, commercial samples were used and no details for these were available. Besides the numerical purity values, the source and/or method of synthesis of the sample as also the number and kinds of purification procedures employed were also studied in order to assess their effect on the purity of the substance.

For the more common halomethanes, several sets of numerical values were invariably available. Initial screening on the basis of accuracy of measurement and purity of the sample usually eliminated some of the values. Thereafter, some of the other above criteria were used to decide whether to eliminate some more values and to assign additional weightage to certain highly reliable data points. While quantitative information on the accuracy of measurement, sample purity, etc. was always sought, in some cases these were not available. It was then necessary to evaluate the data of different investigators on an empirical rating of the purification process and the method of measurement used. In order to develop a rating of the measurement techniques, we have relied primarily on the information provided by Weissberger (187). With an accuracy of $\pm 0.000005 \text{ g cm}^{-3}$

in density, the pycnometer is probably the most accurate and widely used apparatus. Almost of the same accuracy is the hydrostatic weighing method; the totally immersed hydrostatic balance however has, according to Weissberger, an estimated accuracy of ± 0.00003 . Volume changes correct to $\pm 0.000003\%$ are measurable by good dilatometers, thereby ranking these on par with pycnometers. By contrast, the float technique results in errors as high as ± 0.001 . To some extent, the investigator's past reputation did influence the weightage assigned to his data.

The emphasis has been to select the data as a function of temperature of liquid in air and for the saturated liquid regions. Initially certain data were selected based on sample purity, method and accuracy of measurement, care with which the experiments were carried out, reproducibility of data, and reputation of authors. Other data were selected after "matching", by inspection, with the above accurate values. For example, the data of Timmermans at 0° , 15° and 30°C , and of Dreisbach and Martin at 20° and 25°C formed an important basis in selecting the other data. These data were then carefully analyzed to see the general trend over the entire temperature range and to check if each selected data point "fitted" with other points in representing a systematic behavior. In certain cases where there was some doubt about the consistency of the data, the density versus temperature plots were prepared to help the selection of "best" data.

In some cases, we have had to rely entirely on the author's past reputation. In order to smoothen the data and to check gross inconsistencies among the data points, the following mathematical models were chosen to fit the data. Linear least squares regression on IBM 7044 computer at IIT-Kanpur was used in each case.

1. For data up to the boiling point

$$d = a + bT + cT^2 + dT^3 + \dots$$

2. For data up to the critical point, the Martin equation:

$$d - d_c = A(1-T_r)^{1/3} + B(1-T_r)^{2/3} + C(1-T_r)^{3/3} + D(1-T_r)^{4/3} + \dots$$

Depending upon the accuracy of the experimental data, the average and maximum errors tolerable in regression were normally fixed at $\pm 0.0001 \text{ g cm}^{-3}$ and $\pm 0.0005 \text{ g cm}^{-3}$. The final selected density values in the form of an equation were assigned an uncertainty based upon the "maximum error" in the final regression. Whenever available, the values of Timmermans and coworkers, and of Dreisbach and Martin are recommended as the "best" values for the stated temperature range.

An explanation of the errors referred to is necessary. In this report, two kinds of errors are discussed:

- (a) Those inherent in the property measurements, and
- (b) Those resulting from the regressions.

We have used the average absolute error rather than the simple average error, since this eliminates the possibility of large positive and negative errors nullifying to give a misleading representation. However, the error distribution was still considered while rejecting specific data points during the regressions. The average absolute error thus served primarily to gauge the merit of the regression in its entirety and resulted in en bloc rejection of the fluoromethane regression. Data giving more than twice the standard deviation were "suspect" and were checked again for their reliability. This criterion implies a 95% confidence in our regression equations, assuming the errors are normally distributed. Concurrent with this procedure of selective elimination of "bad" data, agreement with reliable values at 20° and 25°C was also ascertained.

While in the discussions for individual compounds, reference has been made primarily to the calculated values from 15° to 30°C, the regression constants have also been used to obtain densities at 5°C intervals in the regressed temperature range. These computations have two underlying objectives: (i) to compare the calculated values at specific temperatures, often substantially away from the region 15° - 30°C, with reputed values at these temperatures. For this comparison, Table 5 lists the details for the temperatures at which the regression errors have been the greatest and the

smallest; (ii) to furnish the readers with sets of readily usable data.

Normally when the fit was good, agreement with the most reliable values was excellent. An interesting feature observed during regression was that the values of the regression constants changed considerably after subsequent removal of "bad" points. After removal of supposedly all "bad" points, the regression constants changed slightly when certain "good" points were removed. This procedure of elimination of "bad" points could be considered to yield stable and correct final values. Table 2 gives the summary of regression results for each compound. Where possible, the TRC values have been mentioned in paranthesis. To illustrate the reliability of regression, the number of data points regressed was also included in each case. In order to give an overall picture of the regression results, deviation plots of density versus temperature are reported for each compound.

There are a number of ways of checking our procedure of selecting the "best" values and of regressing the selected data to a model. One way is to give deviations at each point in a tabular form for each compound. We have chosen the following procedure. The difference between the selected or regressed and the corresponding experimental density value is plotted versus temperature for each compound over the entire temperature range as "deviation plots". This gives

an overall picture of the randomness of the fit and the magnitude of the deviations. In addition, Table 3 reports the temperatures T_1 and T_2 at which the deviations are the maximum and minimum, respectively. This is a check to see whether the largest deviations are at the extreme points. If this happens, then that particular regression is not good. Table 5 gives a comparison at rounded temperatures including the highest and the lowest regression temperatures with reliable experimental data e.g. TRC, Timmermans, Dreisbach and Martin, etc.

The detailed discussion for each compound follows:

FLUOROMETHANE (CH_3F)

Very limited data are available and pertain primarily to the saturated liquid region. Cawood and Patterson (1932) have reported data over a limited temperature range ($20^\circ - 45^\circ\text{C}$) for two samples purified by repeated fractionation. The temperatures for both samples overlap but the densities differ appreciably. For example, $d^{30.02} = 0.5290 \text{ g cm}^{-3}$ and 0.5332 g cm^{-3} , and $d^{43.0} = 0.4204 \text{ g cm}^{-3}$ and 0.4063 g cm^{-3} . Since no experimental accuracy, sample purity, etc. are mentioned it is difficult to choose between the two sets of data and hence these data were not selected. Gross, et. al. (1940) have used the dilatometric method for measuring low

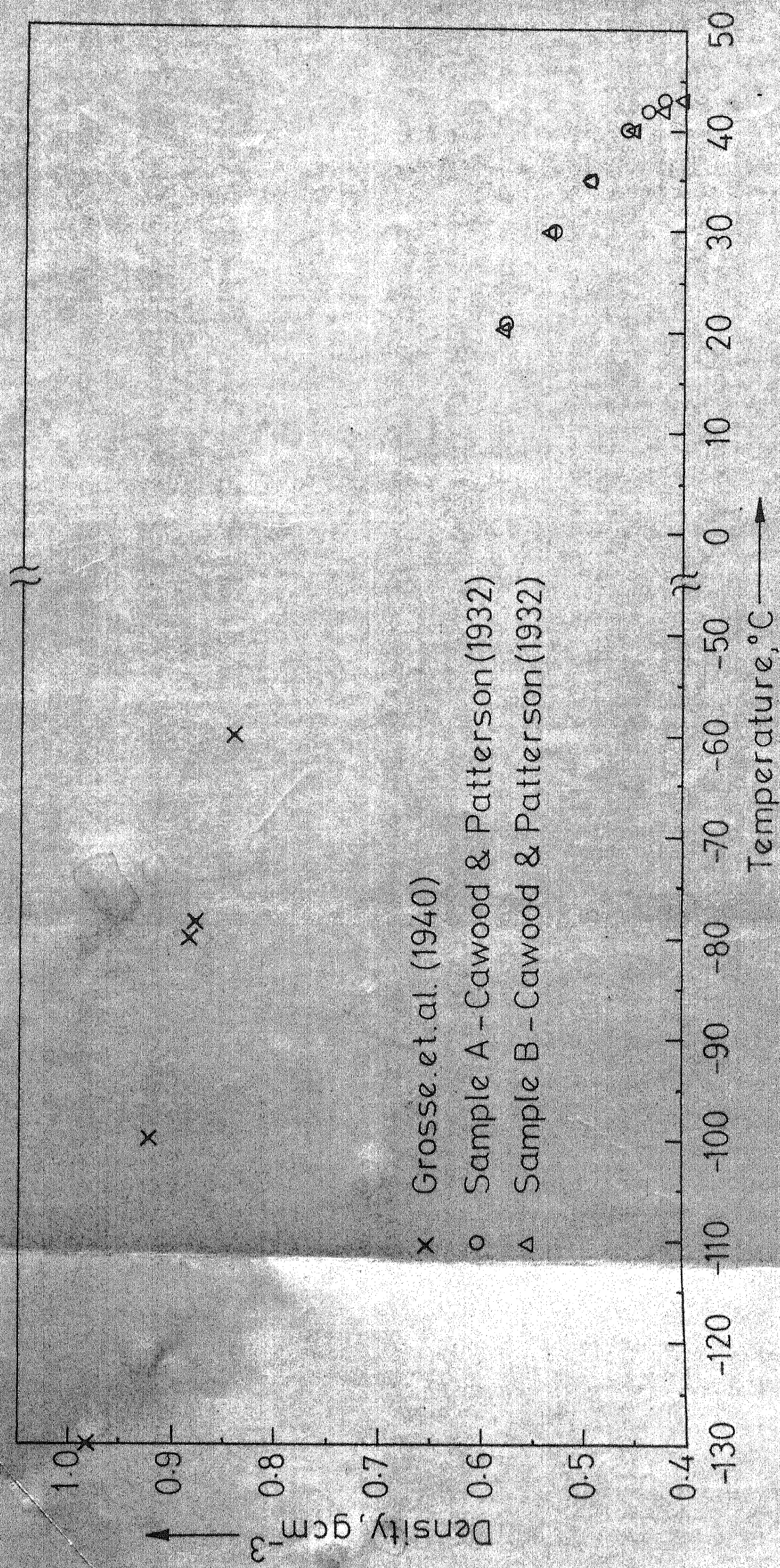


Fig.1 - Density - Temperature Plot for Fluoromethane(SL).

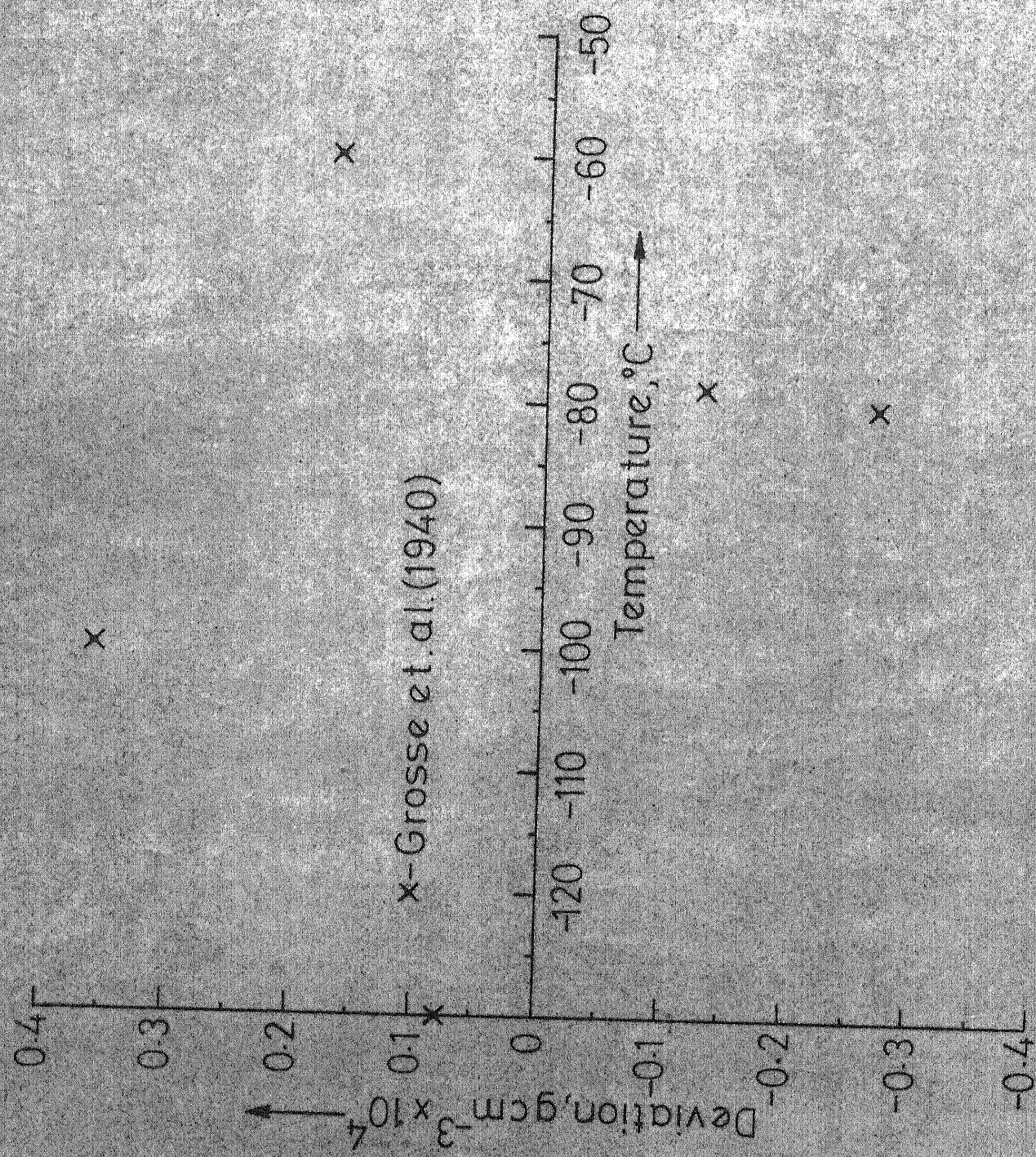


Fig. 2 - Deviation Plot for Fluoromethane (SL).

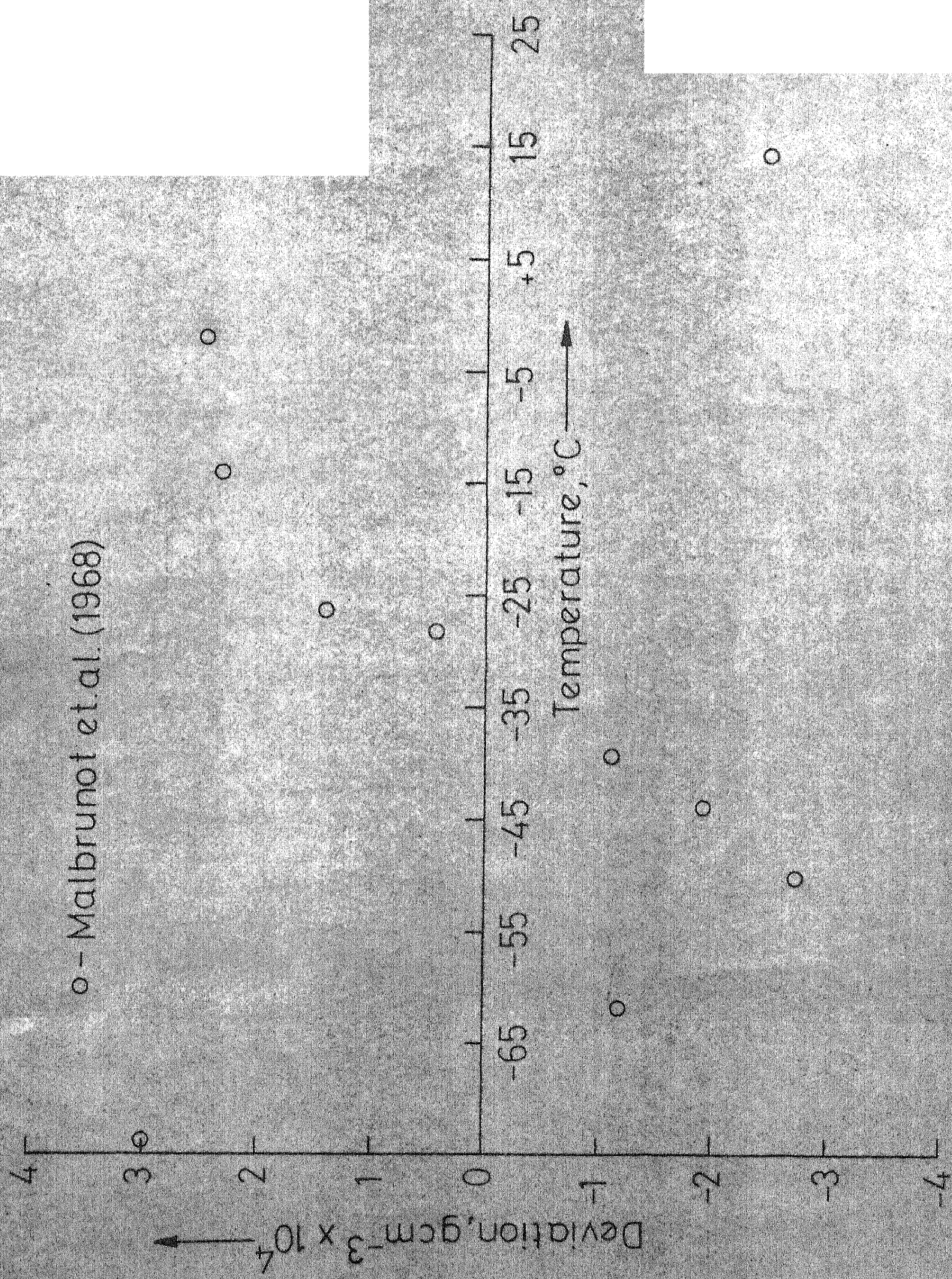


Fig. 3 - Deviation Plot for Fluoromethane (L).

temperature densities (-130 to -60°C). The available data were plotted, as shown in Fig. 1 and no systematic trend was observed. Since data in the temperature range (-60° to $+20^{\circ}\text{C}$) bridging the regions of Grosse and Cawood are not available, it is difficult to assess convincingly the merits of each set of data. The data of Grosse, et.al. were selected for the low temperature region. These data were regressed to quadratic and cubic equations quite satisfactorily. We suggest, therefore, that the equation reported in Table 2 be used for interpolation within the temperature range -130° to -50°C with an accuracy of $\pm 0.0001 \text{ g cm}^{-3}$ in the calculated value.

DIFLUOROMETHANE (CH_2F_2)

Data for this compound are available only from Malbrunot, et. al. (1968). They used a 99.90 mole% pure sample and presented carefully measured saturated density values from -73° to $+14^{\circ}\text{C}$, using the float technique. These are the only reliable data available and are selected. Regression with the polynomial equations indicated that the deviations by the quadratic model were all positive. The deviations were, however, more random with the cubic model. The average errors of ± 0.0002 were almost the same by the two models. On the basis of randomness of the errors, the cubic equation was selected for interpolation purposes. Densities calculated at 20° and 25°C are 1.0311 and 0.9897 g cm^{-3} .

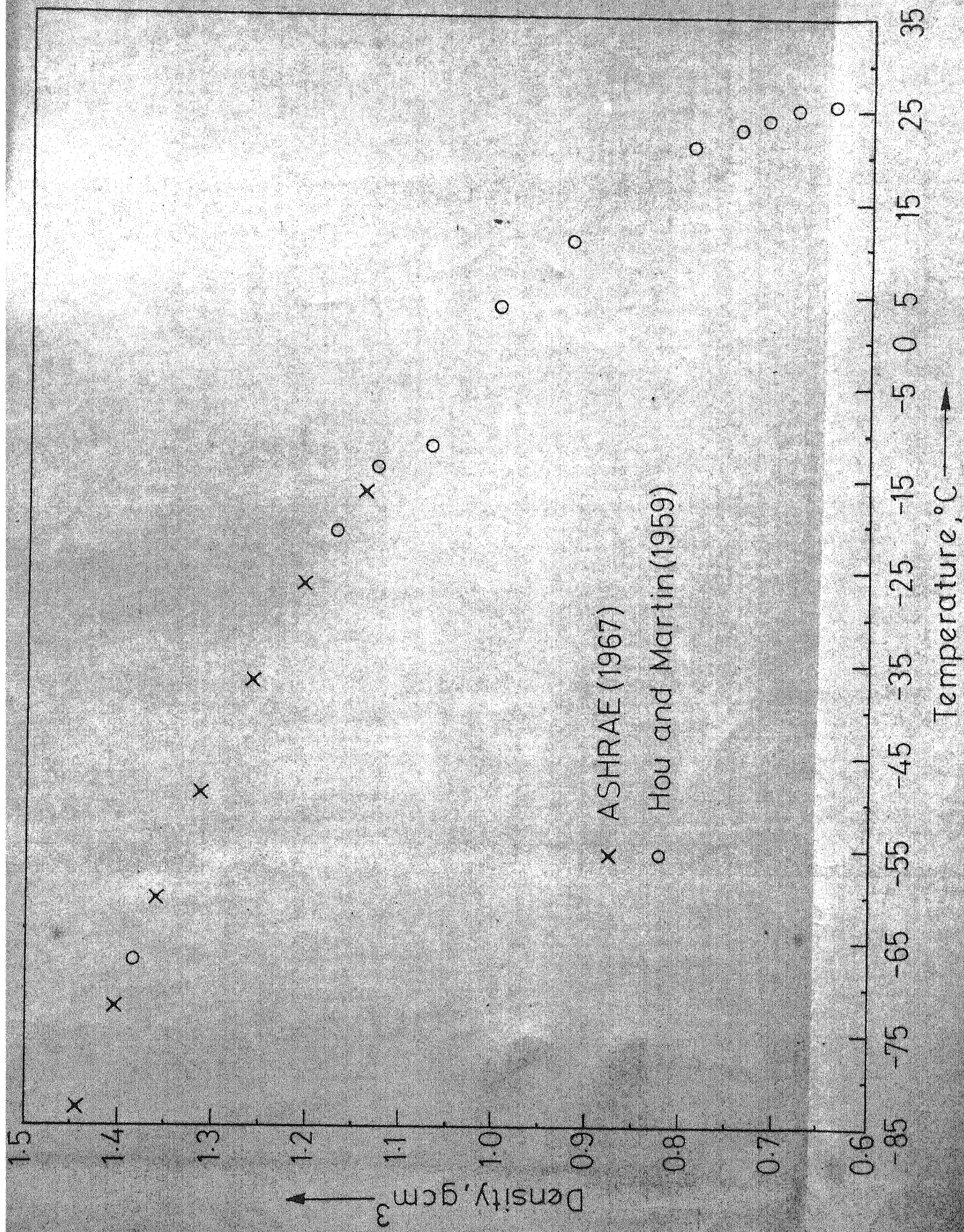


Fig. 4 - Density - Temperature Plot for Trifluoromethane (SL).

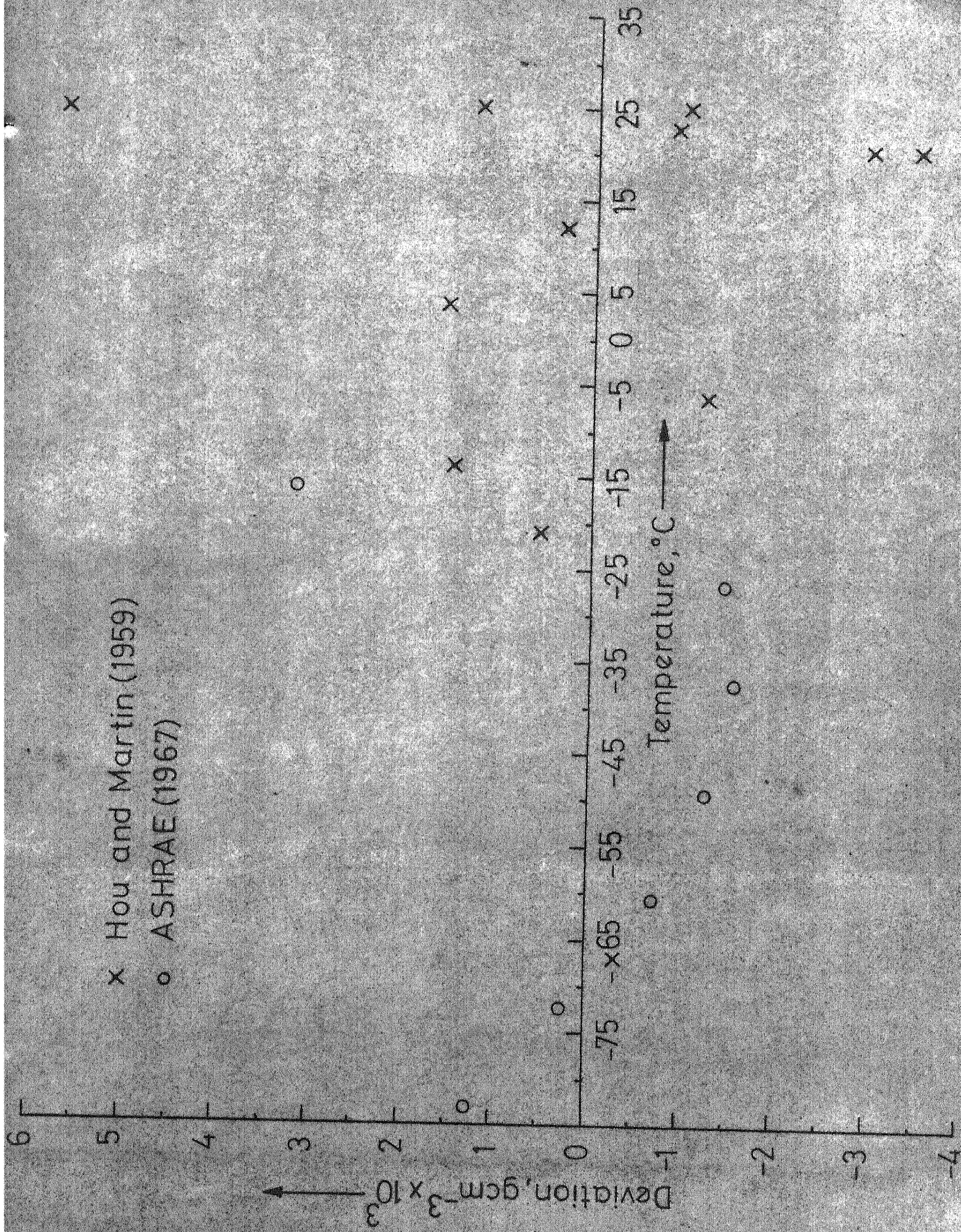
respectively. These values are appreciably different from the T.R.C. value of 0.80 g cm^{-3} , selected much earlier. However, the calculated values agree well with Malbrunot, et. al's data, as shown below:

| <u>Temp., °C</u> | <u>$d_{\text{cal.}} \text{ g cm}^{-3}$</u> | <u>$d_{\text{expt.}} \text{ g cm}^{-3}$</u> |
|------------------|---|--|
| - 61.79 | 1.6775 | 1.6776 |
| - 39.43 | 1.5044 | 1.50415 |
| - 2.11 | 1.2106 | 1.2104 |

Therefore, we recommend our equation for the range -60° to $+25^\circ\text{C}$, assigning an accuracy of ± 0.0003 to the calculated value.

TRIFLUOROMETHANE (CHF_3)

Hou and Martin, in 1959, and ASHRAE (1967) reported density data for the saturated liquid, the former from -67° to $+25^\circ\text{C}$ and the latter from -83° to -16°C . Hou and Martin did not mention the experimental accuracy but their repeated fractionation indicates high purity of the sample used for the investigation. They used the float technique for the measurements. Based upon the measurement technique the data are assigned an accuracy of $\pm 0.0005 \text{ g cm}^{-3}$. ASHRAE's values are reported for a 99.90 mole % pure sample, but no other details are available. Both ASHRAE and Hou and Martin data were selected for the analysis and are shown in Fig.4. Since the data upto the critical point were available, the Martin equation was tried. Martin's data,



especially in the temperature region 3° to 25°C, were observed to result in deviations as high as 0.008 g cm⁻³. Anticipating that ASHRAE's values have tended to "cloud" Martin's data in the subzero range, so that agreement of the regression equations in the extended range till 25°C becomes distorted, the two sets of data were regressed separately. The ASHRAE regression did indicate some improvement. But until better data become available, the combined regression is recommended with the explicit caution that errors of the order of 0.005 may be expected. Representative results are given below for assessment:

| <u>t, °C</u> | <u>d_{calc.}, gcm⁻³</u> | <u>d_{expt.}, gcm⁻³</u> | <u>Reference</u> |
|--------------|--|--|------------------|
| -72.30 | 1.4059 | 1.4056 | 3 |
| -20.85 | 1.1705 | 1.1700 | 73 |
| 23.02 | 0.7433 | 0.7443 | 73 |

TETRAFLUOROMETHANE (CF₄)

Liquid density data are very scanty. As early as 1930, Ruff and Keim used a fractionally distilled sample for measurements at -180°, -118° and -132°C. In subsequent years further values at the same temperatures have been reported but experimental details are lacking and data are reported to only three significant figures. No liquid density selection has therefore been made. For the saturated liquid, Knobler, et.al.(1964) reported two values (at -177.11° and -173.13°C),

but by far the major sources of data are Knobler and Pings (1965), from -179.43° to -122.72°C , and Abbiss, et. al. (1965), from -180.79° to -114.74°C . Knobler and Pings used the pycnometric method for a 99.74 mole% pure sample and obtained density data accurate to $\pm 0.1\%$ (accuracy of $\pm 0.001 \text{ g cm}^{-3}$). No details are available for the data of Abbiss and coworkers. However, their region of experimentation overlaps that of Knobler and Pings, and agreement at specific temperatures indicates the reliability of Abbiss' data. Both sets of data were selected for further scrutiny and regression. Initial regressions also used the two values of Knobler, et al (1964) but these were subsequently discarded owing to large deviations. At -179.43° and -161.35°C (Knobler and Pings) deviations of the order of 0.001 were obtained, while at other temperatures they ranged from 0.0001 to 0.0009. These are shown in Fig.6. As the experimental accuracy of Knobler and Pings' data is ± 0.001 , the above regression was chosen as final. The quadratic model is recommended for the temperature range -180° to -100°C , assigning an accuracy of $\pm 0.001 \text{ g cm}^{-3}$ for the calculated densities. Results for selected temperatures illustrate our observations.

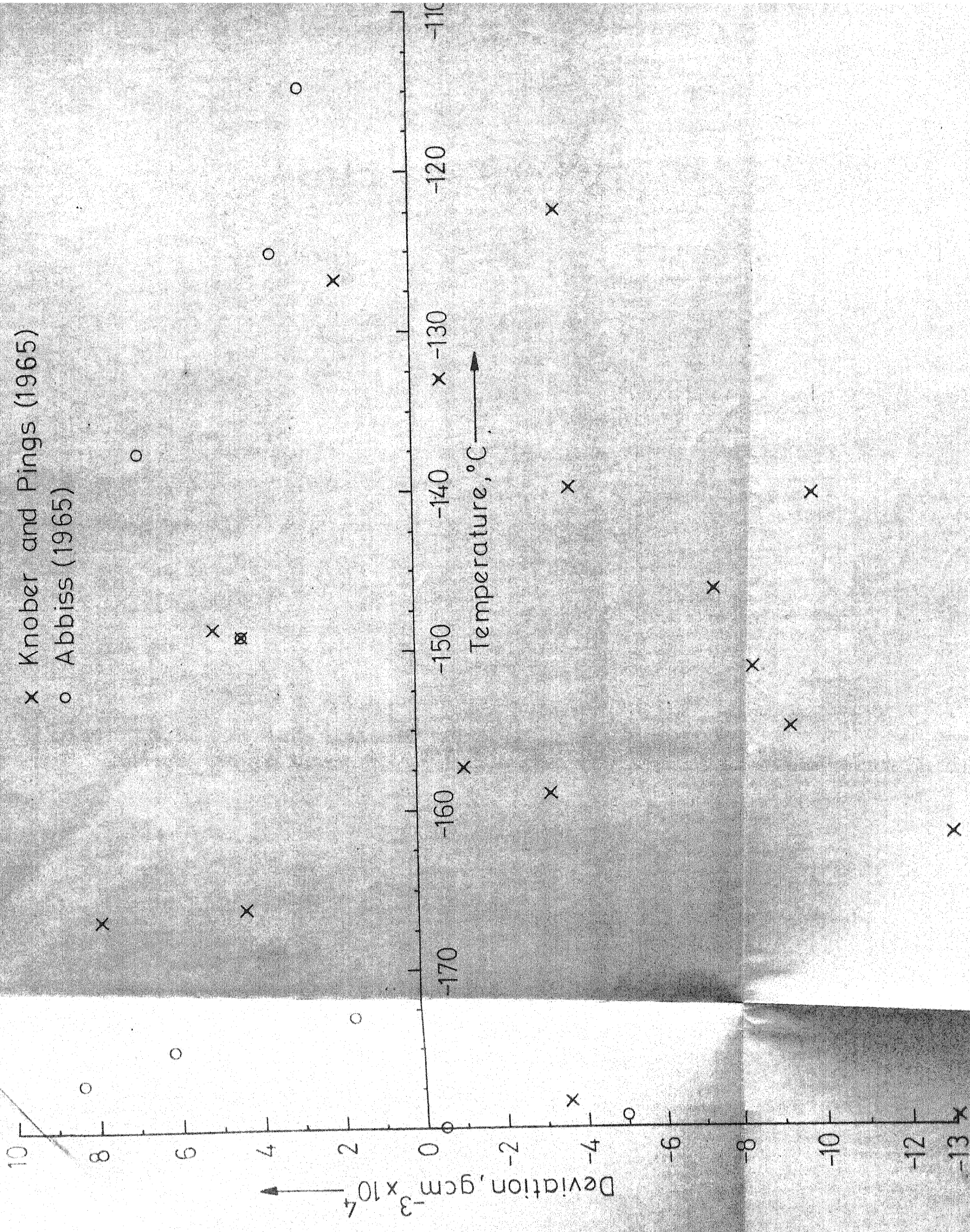


Fig 6 - Deviation Plot for Tetrafluoromethane (SL).

| <u>t, °C</u> | <u>d_{calc.}, gcm⁻³</u> | <u>d_{expt.}, gcm⁻³</u> | <u>Reference</u> |
|--------------|--|--|------------------|
| -173.13 | 1.8360 | 1.8360 | 1 |
| -146.20 | 1.7053 | 1.7060 | 85 |
| -125.14 | 1.5973 | 1.5970 | 1 |

Extrapolation of the regression equations to 25°C is obviously inadvisable; hence the T.R.C. values may be used for 20° and 25°C.

CHLOROMETHANE (CH₃Cl)

The only extensive work for liquid density is that of Morgan and Lowry (1930). For a sample purified by distillation, dilatometric measurements were made for the temperature range -90° to -20°C and the values reported have been interpolated at 10° intervals. Two pycnometric values, both at -23.73°C, are available separately from Bowden and Jones (1948), and Nodiff, et. al. (1953), both of whom obtained the identical value of 0.9915 g cm⁻³. No accurate set of data has been reported in any subsequent work. The values given by Morgan and Lowry (1930) were selected and were found to fit a quadratic polynomial with an average error of ± 0.0002 g cm⁻³ which is below the experimental uncertainty. This fit is recommended in the temperature range of -90° to -20°C with an estimated accuracy of ± 0.0006 g cm⁻³ in the calculated value.

o - Morgan and Lowry (1930)

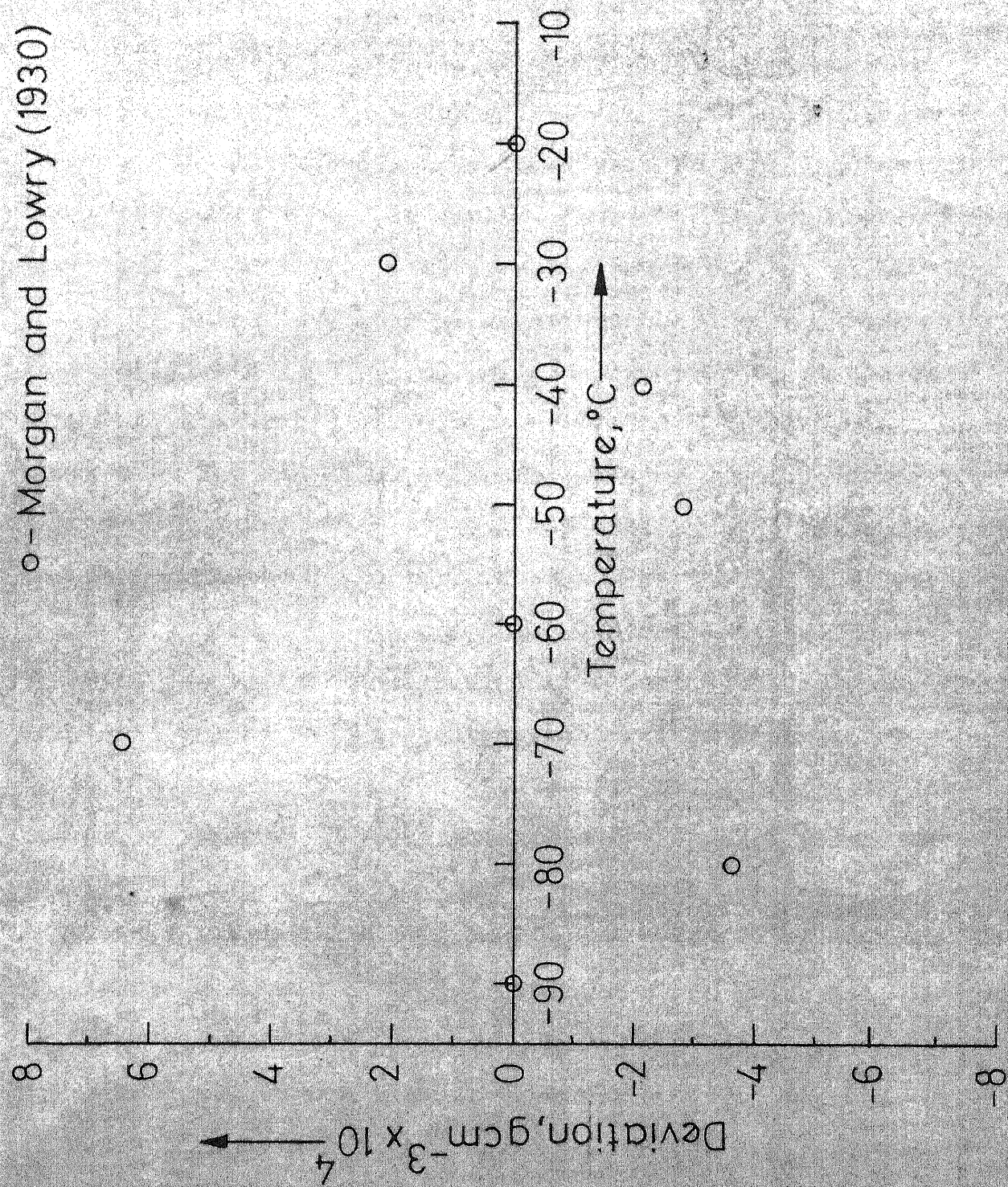
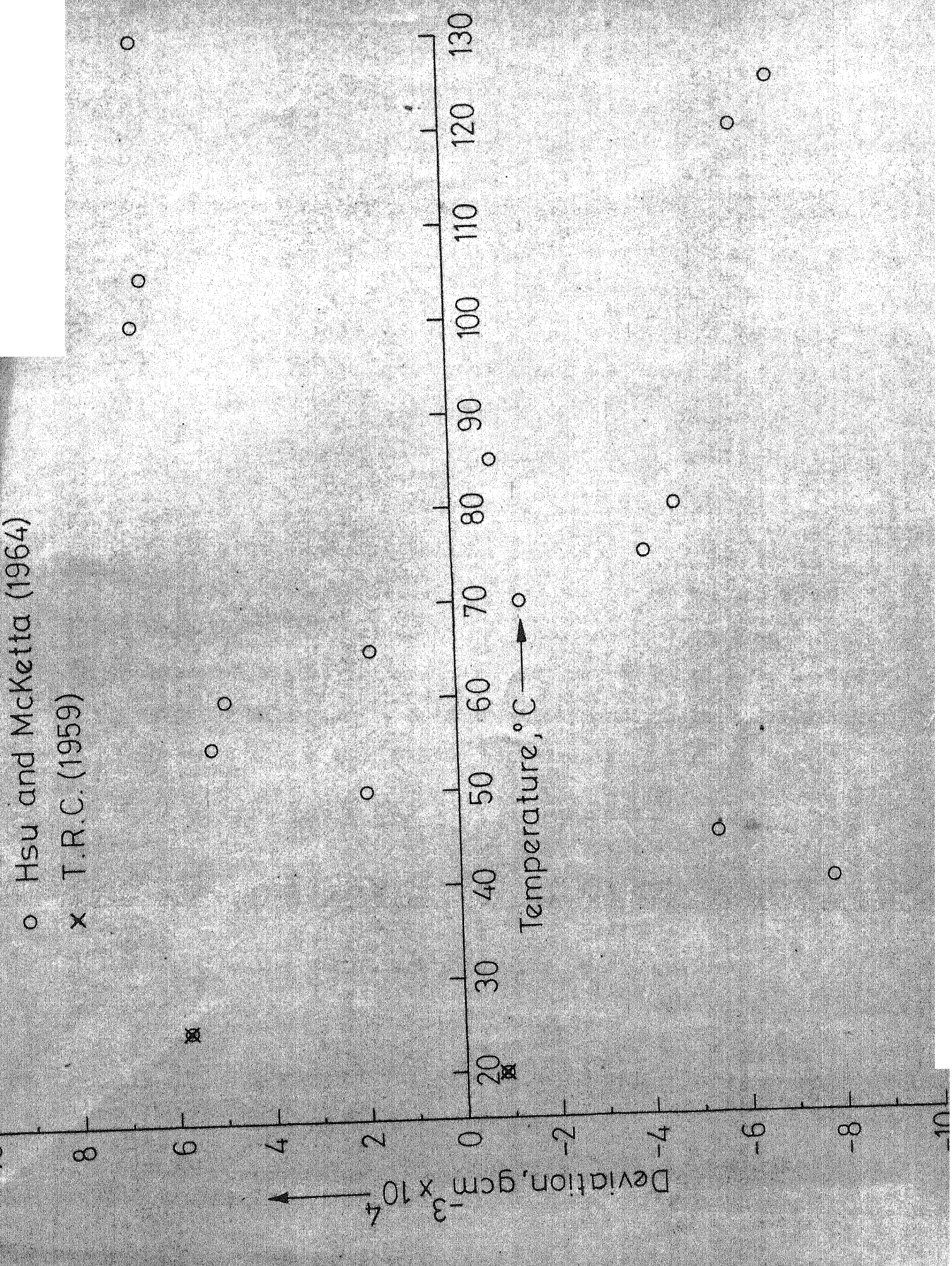


Fig.7 - Deviation Plot for Monochloromethane (L).

The earliest data for the saturated region are from Holst (1914) covering the range -40° to $+40^{\circ}\text{C}$ at 5° intervals. Tanner, et. al. in 1939, also reported saturated liquid densities (from -40.0° to $+76.6^{\circ}\text{C}$) but with inadequate experimental details. One may note, however, that at -40°C and $+60^{\circ}\text{C}$ Tanner's values of 1.031 and 0.836 g cm^{-3} compare favourably with 1.032 , 0.837 g cm^{-3} , reported by Ritter in 1958. A wider range of temperature ($+35^{\circ}$ to $+140^{\circ}\text{C}$) is covered by Hsu and McKetta (1964), whose four-place density data were obtained for a 99.9 mole% pure sample. Based on the sample purity and overall accuracy of the reported values, the data of Holst (1914) and Hsu and McKetta (1964) were selected for further analysis. The selected values were regressed to the Martin equation. The values reported by Holst resulted in errors beyond the largest specified. The rejection of some of these data points did not improve the fit perceptibly and hence Holst's data were removed completely. They were retained in the preliminary analysis because Holst's data extended beyond Hsu and McKetta's data in the low temperature region. Ultimately only Hsu and McKetta's data were selected. The final Martin regression of Hsu and McKetta's data yielded an average error of 0.0005 g cm^{-3} . Hsu and McKetta have themselves furnished polynomial correlations for $(d_l + d_g)$ and $(d_l - d_g)$; from these two they calculated saturated liquid densities from 35° to 140°C .

○ Hsu and McKetta (1964)

× T.R.C. (1959)



However, while their values result in errors in the range of 0.27% to +0.26%, our equation is accurate to within $\pm 0.1\%$, and is therefore preferred to the earlier equation. This model gives 0.9158 and 0.9071 g cm⁻³ at 20° and 25°C respectively. These values agree reasonably well with the 1959 selected T.R.C. values of 0.9157 and 0.9065 g cm⁻³ respectively.

DICHLOROMETHANE (CH₂Cl₂)

A host of authors have reported liquid densities. The most extensive set of values, from -100° to +40°C, is furnished by Morgan and Lowry, who, in 1939, used an Eastman-Kodak sample and the dilatometric method for density measurements accurate to four significant figures. Timmermans and Hennaut - Roland (1932) reported the following data.

| <u>t, °C</u> | <u>d, gcm⁻³</u> |
|--------------|----------------------------|
| 0 | 1.36174 |
| 15 | 1.33479 |
| 30 | 1.30777 |

The following values are available at 20° and 25°C.

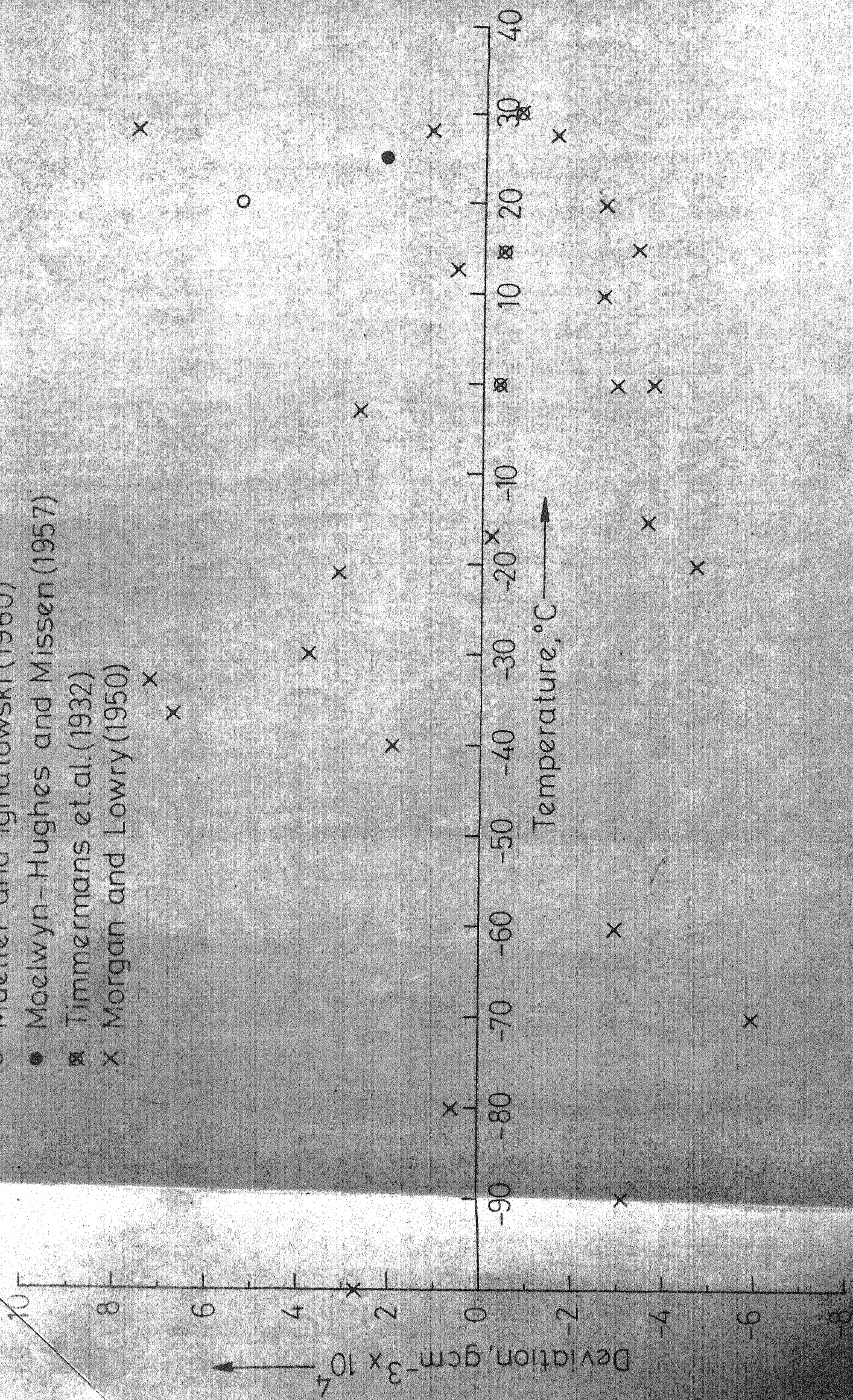
| <u>20°C</u> | | <u>25°C</u> | |
|----------------------------|---------------------------|----------------------------|-------------------------------|
| <u>d, gcm⁻³</u> | <u>Author</u> | <u>d, gcm⁻³</u> | <u>Author</u> |
| 1.3255 | Eftring (1938) | 1.3181 | Davis et.al.(1939) |
| 1.3283 | Mumford, Phillips(1950) | 1.3169 | Barclay, Lefevre (1950) |
| 1.3252 | Mueller, Ignatowski(1960) | 1.3160 | Griffing, et.al.(1954) |
| | | 1.3165 | Moelwyn-Hughes, Missen (1957) |

Most of the authors used purified samples but did not give any other details except for Griffing who used a 98 mole% sample and Mueller and Ignatowski who used a sample of 99.99 mole% purity using pycnometric method.

No extensive and reliable data are available prior to 1970 for the saturated liquid. Dzung (1948) reported some values, from -30° to $+70^{\circ}\text{C}$, at rounded temperatures, followed later by Riedel (1954). The most recent and accurate data are from Phillips and Murphy (1970), whose painstaking measurements by the float technique for a 99.9 mole% pure sample yielded reliable values from -64.77° to 100.78°C .

The liquid densities of Morgan and Lowry are not as accurate as those of others (uncertainty estimated to be ± 0.0005 to $\pm 0.001 \text{ g cm}^{-3}$) but because of the large temperature range, they were analyzed further. Timmermans data were assigned an uncertainty of $\pm 0.00001 \text{ g cm}^{-3}$ and are selected as the "best" available at 0° , 15° , and 30°C . Linear interpolation of these values yielded $1.3258 \pm 0.0001 \text{ g cm}^{-3}$ for 20°C and $1.3168 \pm 0.0001 \text{ g cm}^{-3}$ for 25°C . This was done to aid us to select the "best" values at 20° and 25°C . For 20°C , the values of Griffing and of Mueller and Ignatowski were selected, the latter because of very pure sample used for the measurement. For 25°C , except for Davis et.al. other values were selected for further analysis. Hence we have available liquid density data from -100°C to $+40^{\circ}\text{C}$. All

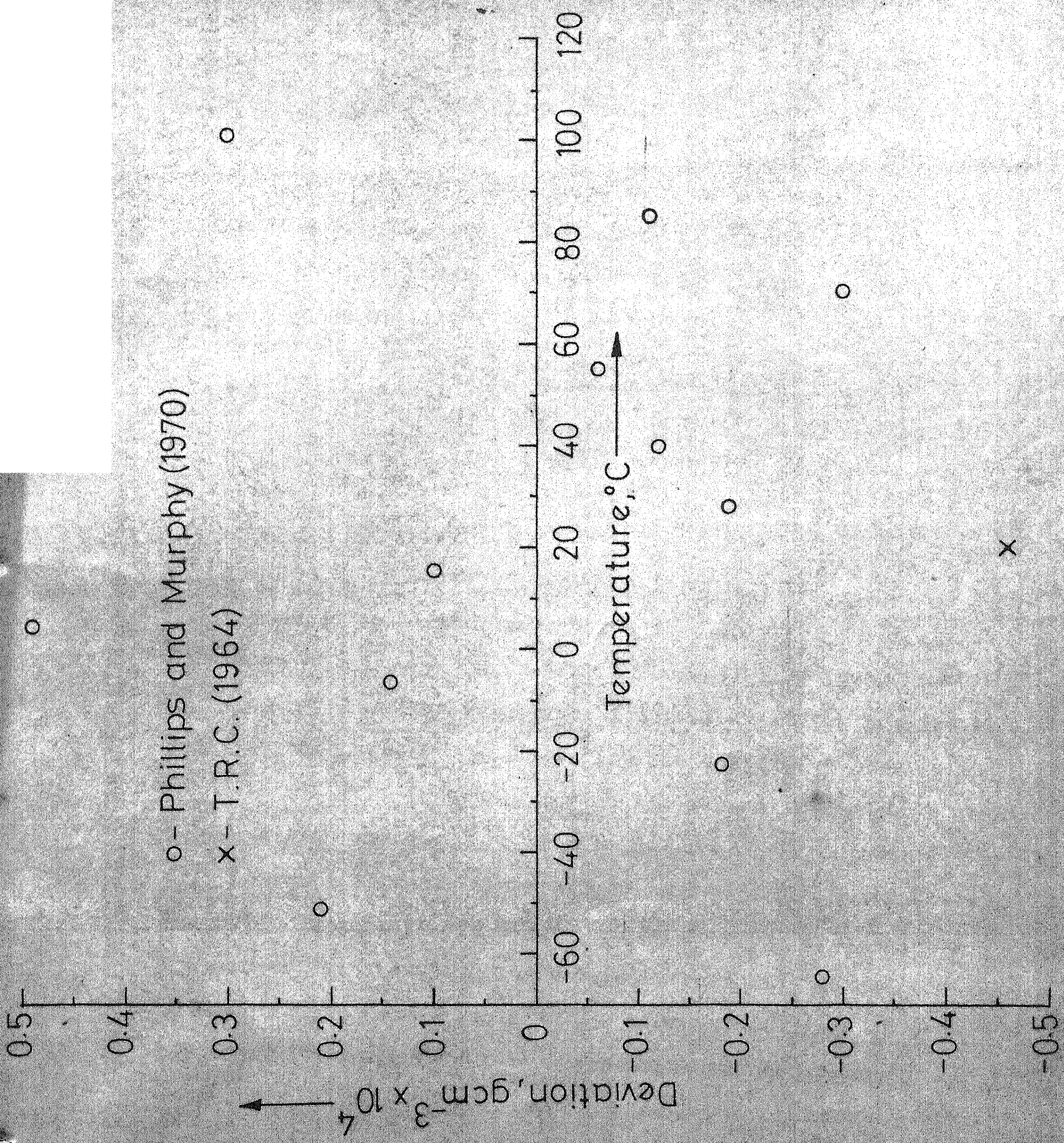
- Mueller and Ignatowski (1960)
- Moelwyn-Hughes and Missen (1957)
- ⊠ Timmermans et al. (1932)
- x Morgan and Lowry (1950)



these selected experimental data (Timmermans interpolated values were not used) were regressed to polynomial models assigning a weightage of five-fold to Timmermans data because of their high accuracy. The desired accuracy was assigned as $\pm 0.0002 \text{ g cm}^{-3}$. Timmermans data were selected as the basis and our regression results were evaluated by comparison with Timmermans values. The elimination of "bad" points (40°C point of Morgan and Lowry) was continued until the calculated values at 0°, 15° and 30°C agreed within ± 0.0002 with Timmermans values. The final regression yielded 1.33474 and 1.30769 at 15° and 30°C respectively, which agree within ± 0.0001 of Timmermans values. Moreover, at 20° and 25°C, 1.3257 and 1.3167 density values were obtained. At 20°C, the agreement is good with Efring but not with Mueller and Ignatowski. At 25°C, the agreement with other experimental values is satisfactory. The regression constants are therefore recommended for the temperature range -100° to + 40°C assigning the following uncertainties.

| <u>Uncertainty</u> | <u>Temperature Range</u> |
|--------------------|--------------------------|
| ± 0.0008 | -100° to - 10°C |
| ± 0.0002 | -10° to + 40°C |

For the saturated liquid, the only reliable data are those of Phillips and Murphy and are selected for further analysis. These fit the cubic model satisfactorily, with an average error of only $\pm 0.00004 \text{ g cm}^{-3}$. This equation is



recommended from -65° to $+100^{\circ}\text{C}$ with an uncertainty in the value of $\pm 0.0001 \text{ g cm}^{-3}$. Agreement of the calculated densities at 20° and 25°C with the T.R.C. values is satisfactory as shown below:

| <u>t, $^{\circ}\text{C}$</u> | <u>d_{calc.}, g cm^{-3}</u> | <u>d_{TRC}, g cm^{-3}</u> |
|---|---|---|
| 20 | 1.3255 | 1.3255 |
| 25 | 1.3160 | 1.3163 |

TRICHLOROMETHANE (CHCl_3)

Generally scattered data are available for the liquid from several authors. Over four periods of time (1909, 1912, 1922, 1926), the last in collaboration with Martin, Timmermans has published density data covering the temperature range -63°C to $+30^{\circ}\text{C}$. Interpolation of the values from 0° to 30°C yields 1.4892 and 1.4798 g cm^{-3} at 20° and 25°C respectively with an assigned uncertainty of $\pm 0.0001 \text{ g cm}^{-3}$. Tyrer (1914) reported six significant figure values from 0° to 55°C using pycnometry technique and a fractionated sample. Morgan and Lowry (1930) covered almost the same temperature range as Timmermans, but their dilatometric measurements are reported at rounded temperatures and are not as "accurate" as Timmermans' values. Of the later workers, full details are available from only Campbell and Chatterjee (1963), whose pycnometric measurements on a distilled commercial sample

yielded a density value of $1.4806 \pm 0.002 \text{ g cm}^{-3}$ at 25°C . A single normal boiling point (61.2°C) density has been reported by Bowden and Jones (1948). The following authors have reported values on purified samples at 20° and 25°C .

| <u>20°C</u> | | <u>25°C</u> | |
|--|-----------------------------|---|----------------------------------|
| <u>d, g cm⁻³</u> | <u>Author</u> | <u>d, g cm⁻³</u> | <u>Author</u> |
| 1.4889 | Mathews (1926) | 1.4794 | Davis et.al.(1939) |
| 1.48913 | Zmaczynski (1930) | 1.4797 | Bowden, Butler (1939) |
| 1.4870 | Iagemann, et.al. (1949) | 1.4798 | Mumford, Phillips(1949) |
| 1.4892 | Mumford, Phillips (1950) | 1.47928 | Hildebrand, et.al.(1950) |
| | | 1.48073 | Brown, Fock (1955) |
| 1.4892 | Rabinovich (1960) | 1.4795 | Moelwyn-Hughes, Missen (1957) |
| 1.4888 | Khabibullaev(1970) | 1.4799 | Koeford, Villadson (1958) |
| | | 1.4806 | Campbell, et.al.(1963) |
| Average 1.4890 ± 0.0002 neglecting Iagemann | | 1.4796 ± 0.0003 neglecting Brown, and Campbell | |

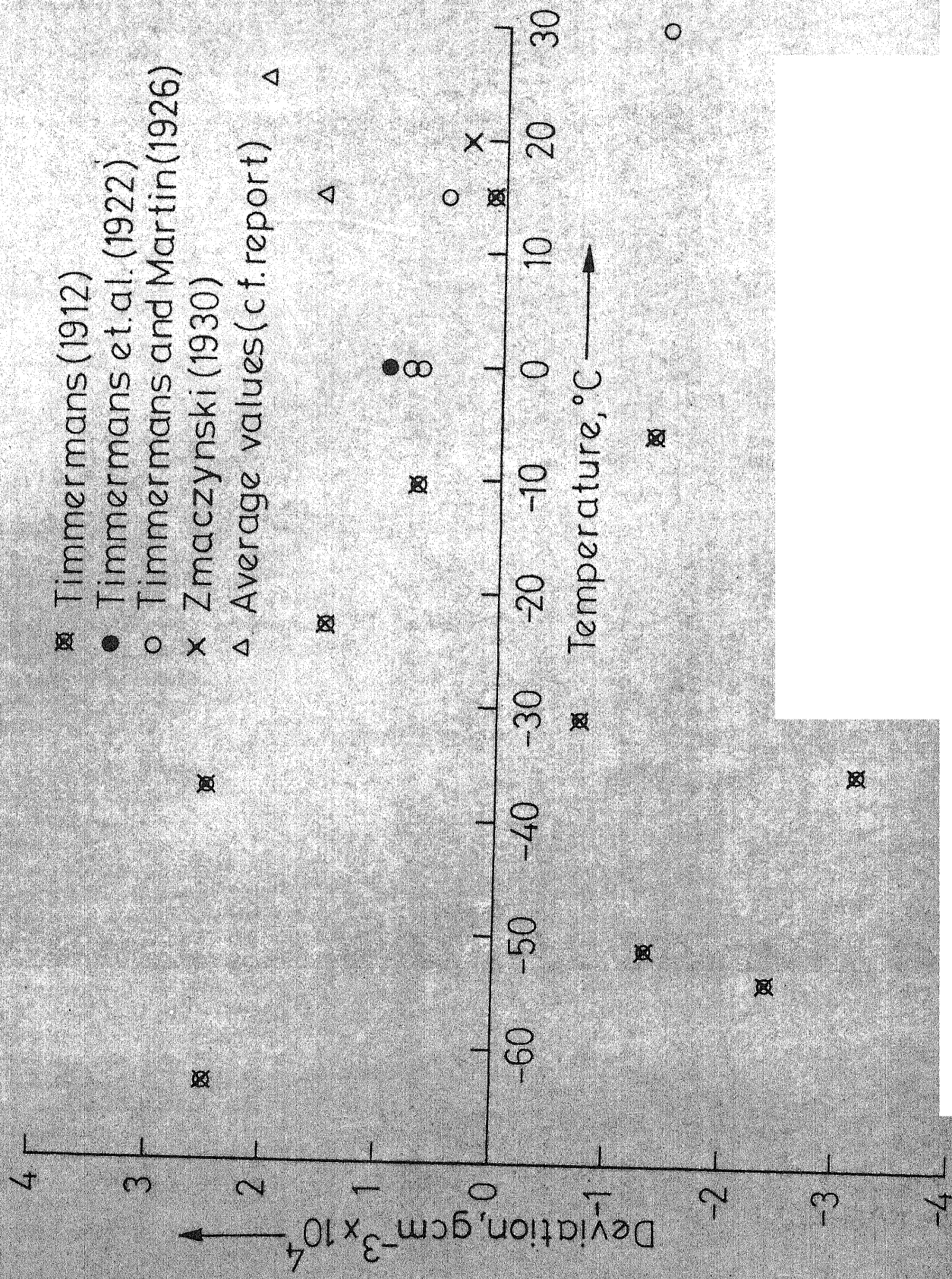
Phillips and Murphy (1970) reported data from -63° to $+80^\circ\text{C}$ which came from the International Critical Tables and are based upon the literature values of Timmermans and others.

For the saturated liquid, an exhaustive set of data for high temperatures (100° to 262.8°C) is provided by Campbell and Chatterjee (1968). Though quantitative information on accuracy is lacking, the data are likely to be

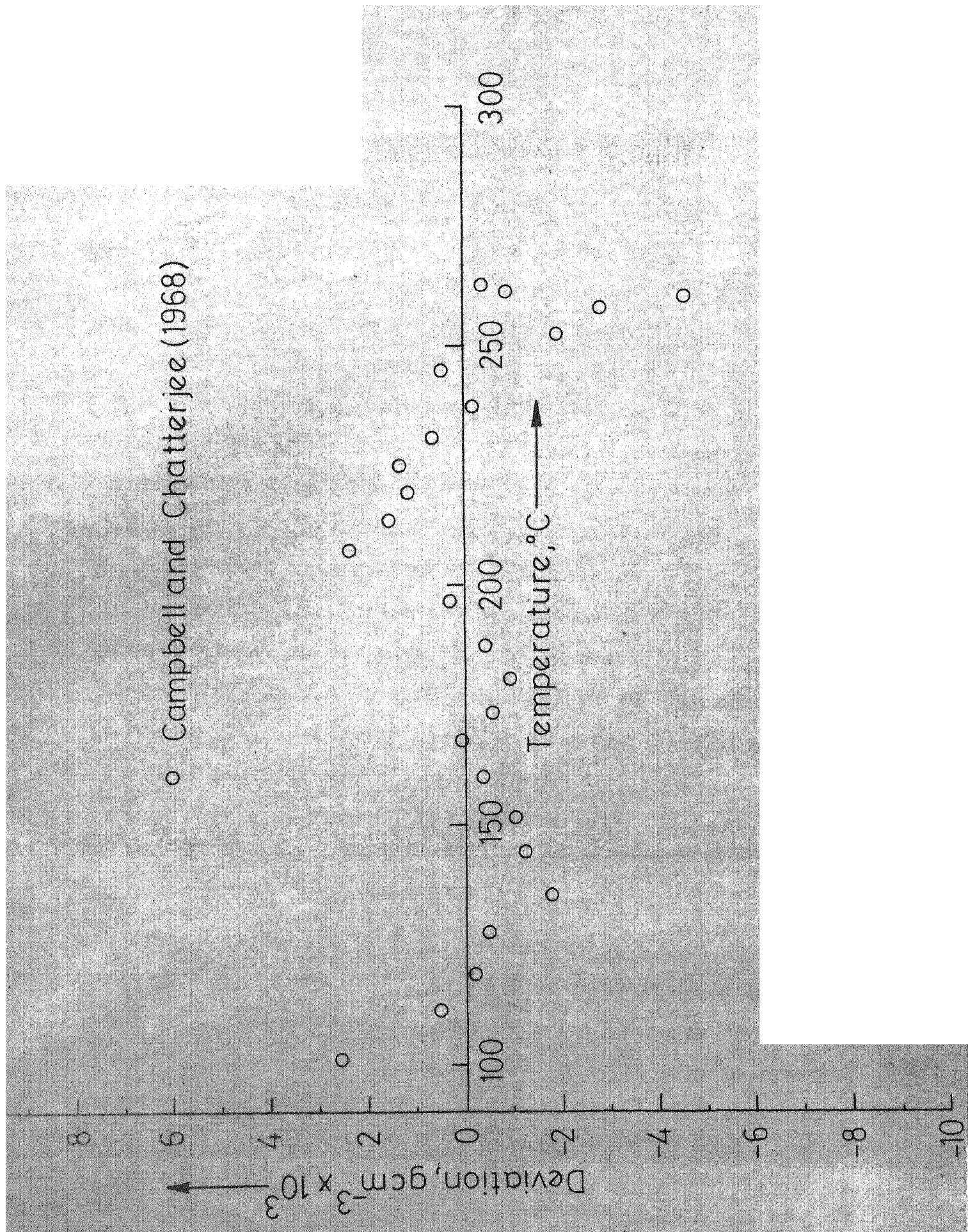
reliable since the pycnometric method was used on a purified sample. They observed slight decomposition of the sample near the critical point.

For the liquid density, we have relied completely on Timmermans data. These were regressed to polynomial models, and the quadratic was found to be satisfactory with an average deviation of ± 0.00014 . The calculated values are 1.4891_6 and $1.4798_2 \text{ g cm}^{-3}$ at 20° and 25°C respectively. The 20° value agrees within ± 0.00003 of Zmaczynski's value and within ± 0.0002 of the average value at 25°C . Hence the regressed constants predict satisfactorily the reliable experimental values within $\pm 0.0002 \text{ g cm}^{-3}$ and are recommended for interpolation and limited extrapolation. The uncertainty in the calculated value is estimated to be $\pm 0.0001 \text{ g cm}^{-3}$.

For the saturated liquid Campbell and Chatterjee's values are the only ones available and are selected. Martin equation was used to represent these data up to the critical point. Surprisingly enough the fit with four and five constants was not satisfactory. The average and the maximum deviations obtained were ± 0.0010 and 0.010 at 262.5°C . The fit could not be improved and it is felt that the data are not of high accuracy. Hence the Martin equation is recommended and an uncertainty of $\pm 0.002 \text{ g cm}^{-3}$ is assigned from 100° to 250°C and $\pm 0.10 \text{ g cm}^{-3}$ from 250°C to the critical point.



o Campbell and Chatterjee (1968)



TETRACHLOROMETHANE (CCl₄)

Extensive data are available for the liquid and the saturated liquid regions. Data for the liquid are available from several authors, most of whom have not furnished adequate supporting information. Moreover, a large fraction of the values are centered at 20°C and 25°C. Among the earliest data are those from Gorke, et. al. (1908) and Patterson and Thomson (1908). In 1914, Tyrer provided good pycnometric density data from 0° to 72.43°C. Accurate as his values appear to be, the reported density of 1.63167 g cm⁻³ is somewhat lower than 1.63255 from Timmermans, et.al. (1932). In the next year, Egerton and Lee (1923) provided six very closely spaced values covering the temperature range 15.67° to 18.26°C. As for several other compounds, Timmermans and Martin (1926) again give accurate density values at 0°, 15° and 30°C as follows.

| <u>t, °C</u> | <u>d, g cm⁻³</u> |
|--------------|-----------------------------|
| 0 | 1.63255 |
| 15 | 1.60370 |
| 30 | 1.57480 |

Later, Morgan and Lowry (1930) covered the range -30° to + 70°C and reported three-decimal data at 10°C interval for an acid-treated sample. Even though the dilatometric method was used by them, comparison of their reported

density of 1.572 g cm^{-3} at 30°C with Timmermans and Martin's values shows a discrepancy of 0.003 g cm^{-3} . In later years a host of authors reported single-point density values, usually at 20°C or 25°C . The reliable ones are given below.

| <u>20°C</u> | | <u>25°C</u> | |
|---|-----------------------------|--|-------------------------------|
| <u>d, g cm⁻³</u> | <u>Author</u> | <u>d, g cm⁻³</u> | <u>Author</u> |
| 1.5939 | Moruo (1933) | 1.58458 | Hubbard (1910) |
| 1.59397 | Dreisbach, Martin (1949) | 1.58413 | Grimon (1929) |
| 1.5937 | Mueller, Ignatowski (1960) | 1.58445* | Zmaczynski (1936) |
| 1.59404 | Nyvlt and Erdos (1961) | 1.58454 | Lefevre, Lefevre (1936) |
| 1.59410 | " " | 1.58414 | Scatchard, et.al. (1939) |
| 1.59400 | " " | 1.58452 | Scatchard, et.al. (1946) |
| 1.59372 | Shraiber, Pechenyule (1965) | 1.58429* | Dreisbach, Martin (1949) |
| | | 1.58438* | Hildebrand, et.al. (1950) |
| | | 1.58435* | Brown, Fock (1955) |
| Av = $1.59403 \pm 0.00006 \text{ g cm}^{-3}$ using Dreisbach, and Nyvlt | | 1.5846 | Moelwyn-Hughes, Missen (1957) |
| | | 1.58437* | Nyvlt, Erdos (1961) |
| | | 1.58436* | " " |
| | | 1.58442* | " " |
| | | Av = $1.58437 \pm 0.00008 \text{ g cm}^{-3}$ using * values | |

Dreisbach and Martin's values stand out as the "best" because they used 99.94 mole% purity sample. Mueller and Ignatowski's value is lower by 0.0003 g cm^{-3} than Dreisbach and Martin

inspite of using a highly pure sample of 99.985 mole% and carrying out the measurements on a bicapillary pycnometer. Very precise and painstaking work of Nyvlt and Erdos resulted in accurate pycnometric values from 20° to 40°C. At each temperature three closely agreeing values are reported. They fitted their data to the following equation:

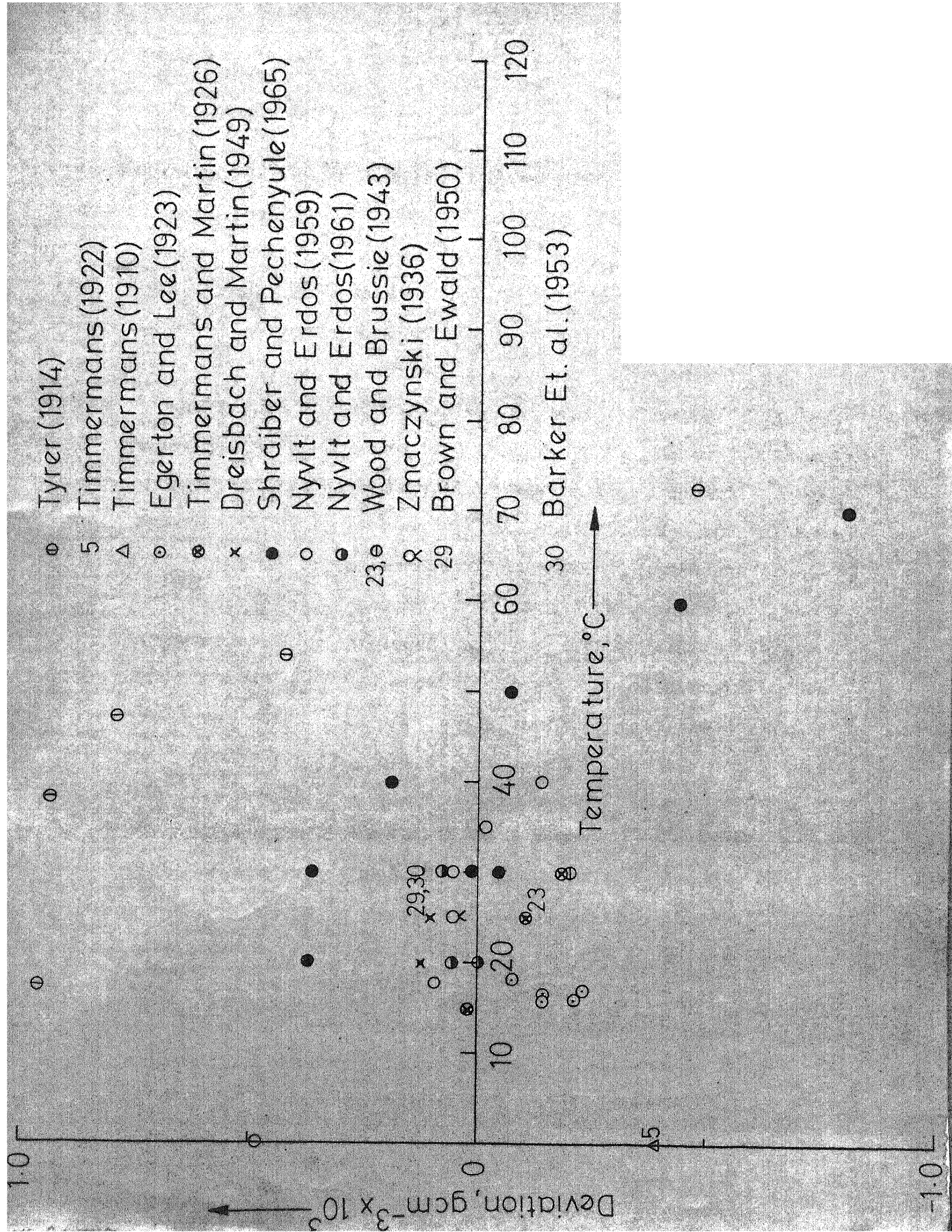
$$d = 1.59406 - 1.935 \times 10^{-3} (t-20) - 1.0 \times 10^{-6} (t-20)^2 \pm 1.2 \times 10^{-5}$$

Shraiber and Penchenyule's values from 20° to 70°C are reported accurate to $\pm 0.00002 \text{ g cm}^{-3}$. They used CCl_4 boiling at 76.7°C with $n_D^{20} = 1.46031$ which should be compared with 76.75°C and $n_D^{20} = 1.46005$ (Dreisbach and Martin). It appears that the sample used by Shraiber and Penchenyule is not as pure as that used by Dreisbach and Martin or Nyvlt and Erdos.

For the saturated liquid, Ramsay and Shields reported high temperature (upto 250°C) densities as early as 1893. Young in 1910, reported data from 0° to 280°C, without any details. The high temperature region has also been explored by Kordes (1954), whose data span the temperature range 79.8° to 282.9°C. The range below that of Kordes has been covered by the later work of Pugachevich, et. al. (1963) who reported pycnometric measurements accurate to $\pm 0.0008 \text{ g cm}^{-3}$ on a distilled sample from 17.2° to 97.9°C. By far the most extensive set of saturated liquid densities with an experimental

accuracy of $\pm 0.0004 \text{ g cm}^{-3}$ has been provided by Campbell and Chatterjee (1969). Employing vacuum distillation to obtain a pure sample, they reported data from 100° to 280°C.

For the liquid density, the data of Timmermans and coworkers from 0° to 30°C, Nyvlt and Erdos, Egerton and Lee, and Shraiber and Penchenyule were selected covering a temperature range of 0° to 70°C and assigning an overall uncertainty of $\pm 0.00001 \text{ g cm}^{-3}$. Out of the 20° and 25°C values available, the averaging procedure yielded $1.59403 \pm 0.00006 \text{ g cm}^{-3}$ for 20°C and $1.58437 \pm 0.00008 \text{ g cm}^{-3}$ for 25°C which were selected as the "best" values. The data from 0° to 70°C were fitted to the quadratic model with an average deviation of $\pm 0.00009 \text{ g cm}^{-3}$. This regression (I) gave 1.59415 and $1.58444 \text{ g cm}^{-3}$ for 20° and 25°C respectively which is beyond the assigned uncertainty. Hence these constants are recommended for 0° to 70°C with an uncertainty in the calculated value of $\pm 0.0001 \text{ g cm}^{-3}$. It was felt that the data from 0° to 40°C were much more accurate (do not cover Shraiber's data) and hence were regressed (II) separately to the quadratic model with an average deviation of $\pm 0.00005 \text{ g cm}^{-3}$. The 20° and 25°C values calculated were 1.59408 and $1.58436 \text{ g cm}^{-3}$ respectively. These values agree very well with the above selected values at these temperatures. Hence for interpolation between 0° to 40°C, the latter regression constants are recommended.



For the saturated liquid, the data of Campbell and Chatterjee were selected as the "best" based on the sample purity, overall methodology, accuracy, etc. The data of Young are old and in general are suspect. The data of Kordes agree reasonably well with those of Campbell. For interpolation purposes, Campbell's data up to the critical were fitted to Martin equation. The values very close to the critical gave deviations of 0.0006 which is larger than the experimental uncertainty and were suspect. Of course it is likely that the Martin equation gives larger deviations near the critical. It is however felt that the experimental data near the critical have a large uncertainty and hence these two points (280.1° and 281.6°C) were discarded. The final regression to the expanded Martin equation gave an average deviation of $\pm 0.0006 \text{ g cm}^{-3}$. It was expected that the fit would be better than what we obtained. Hence the data in general are probably not of very high accuracy. Hence this model is recommended for the temperature range of 100° to the critical with an uncertainty of $\pm 0.0006 \text{ g cm}^{-3}$ in the computed value except near the critical where it is $\pm 0.001 \text{ g cm}^{-3}$.

Another regression was attempted with all available data because of the wider range (from 20° to the critical). With all data fitted to Martin equation an average error of $\pm 0.029 \text{ g cm}^{-3}$ was obtained. This was high and hence the elimination procedure was followed. Certain "bad" data

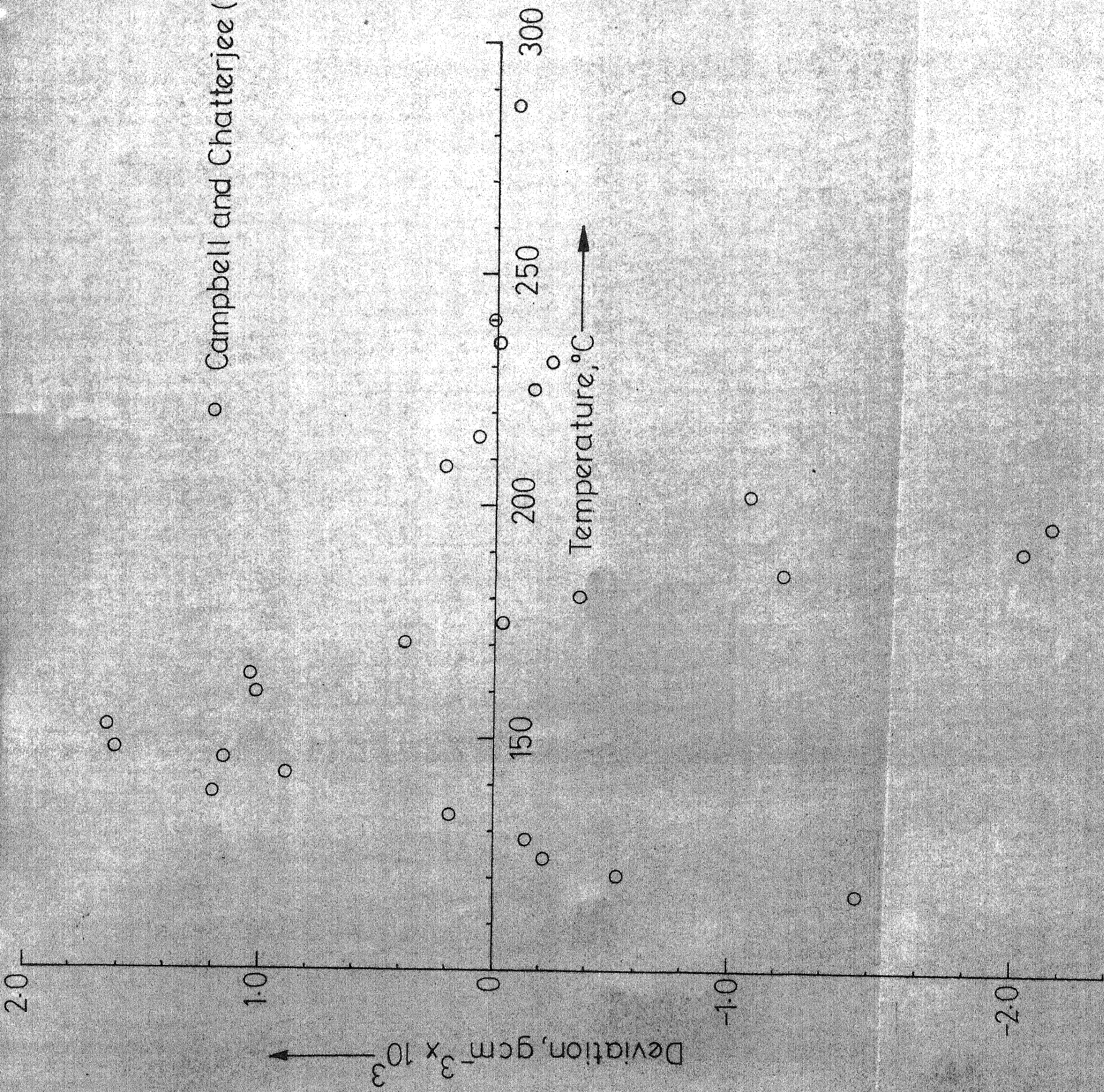


Fig.14- Deviation Plot for Tetrachloromethane(SL).

points were discarded finally yielding an average error of $\pm 0.0006 \text{ g cm}^{-3}$ for the standard Martin equation. This equation is therefore recommended from 20° to the critical point with an uncertainty in the computed value of $\pm 0.0006 \text{ g cm}^{-3}$ except near the critical where it is $\pm 0.001 \text{ g cm}^{-3}$.

BROMOMETHANE (CH_3Br)

Only two values of liquid density, at 4.5°C and 0°C are available, from the dilatometric measurements of Nodiff, et.al. (1953) and from Utermark and Schicke (1963) respectively. Low temperature (-93.6° to $+7.4^\circ\text{C}$) saturated liquid densities are available from Morgan and Lowry (1930). Hsia, in 1931, reported density data for the temperature range -50° to $+50^\circ\text{C}$; he used a purified sample obtained by fractionation and vacuum distillation and reported an accuracy of $\pm 0.5\%$ ($\pm 0.005 \text{ g cm}^{-3}$) in the density measurements. The data, however, are given at 10°C intervals, which suggests interpolation. Both sets of data do not appear to be accurate. Anyway, these are selected as "best" available for further analysis. The quadratic model is recommended which gives an average deviation of $\pm 0.001 \text{ g cm}^{-3}$. The calculated values are assigned an uncertainty of $\pm 0.002 \text{ g cm}^{-3}$ and are compared with the TRC values below:

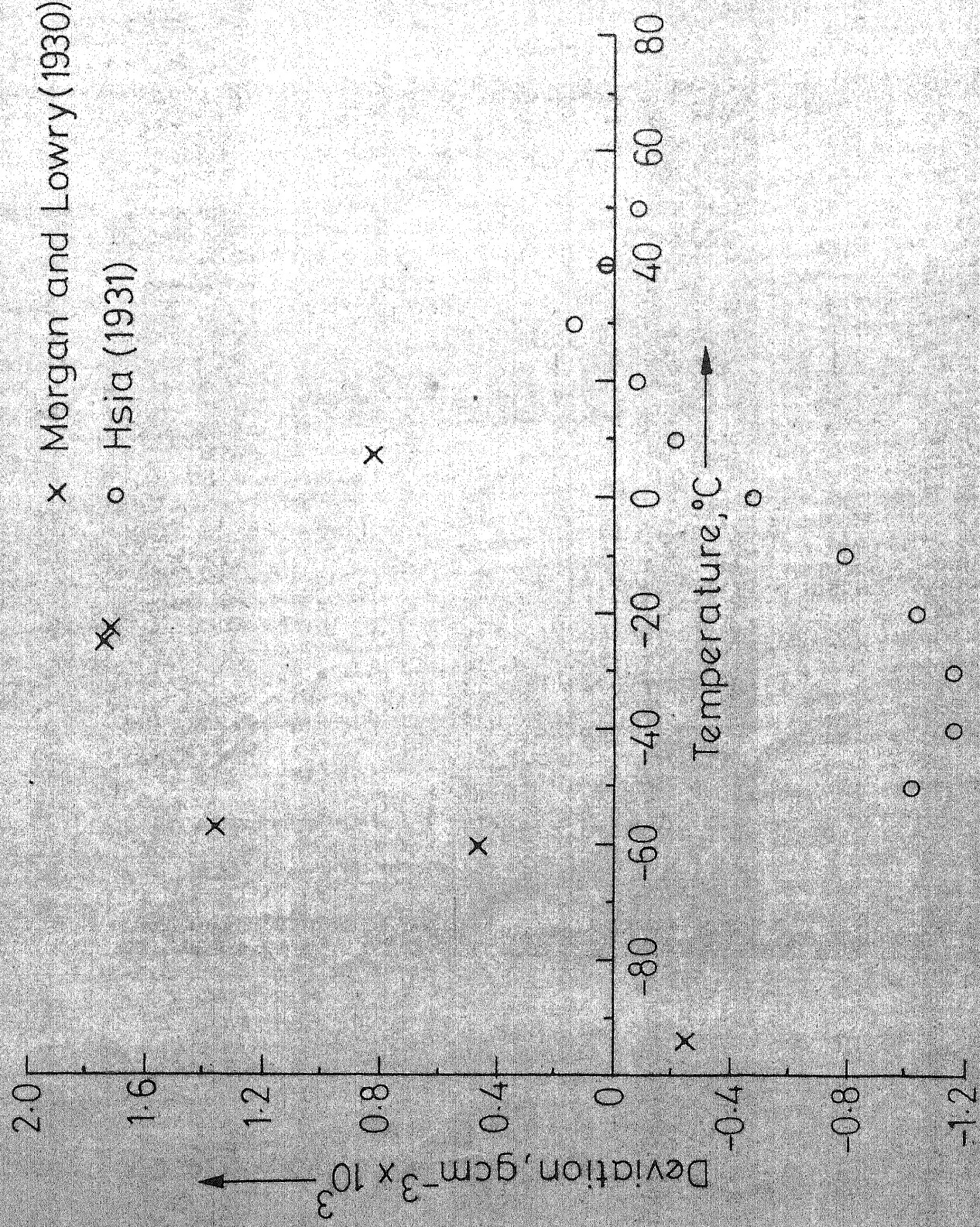


Fig.15 - Deviation Plot for Bromomethane (SL)

| <u>t, °C</u> | <u>d, g cm⁻³</u> | | |
|--------------|-----------------------------|------------|-------------|
| | <u>calc.</u> | <u>TRC</u> | <u>Hsia</u> |
| 20 | 1.6758 | 1.6755 | 1.6769 |
| 25 | 1.6622 | 1.6617 | - |
| 30 | 1.6485 | - | 1.6489 |

DIBROMOMETHANE (CH₂Br₂)

No data are available for the saturated liquid. For the liquid in air, a few data points per author are available from a number of authors. Some have provided supporting details. Mahanti and Das Gupta (1929) report a density of 1.525 g cm⁻³ at 24.85°C by pycnometric measurement on a Kahlbaum sample. A very low temperature (-196°C) value of 2.49 g cm⁻³ is available from Biltz, et.al. (1932). In 1943, Friend and Hargreaves reported data from 18.6 to 97.2°C using the specific gravity bottle method for a distilled sample. Their data were selected in addition to the values of Timmermans and Hennant-Roland (1932) and Griffing, et.al. (1953). The latter's data came from the balance measurements on a 98 mole% pure sample covering the range 0° to 80°C. Thus the selected data covered a range from 0° to 100°C. Timmermans data at 0°, 15°, 30°C are the "best" available and are recommended.

| <u>t, °C</u> | <u>d, g cm⁻³</u> |
|--------------|-----------------------------|
| 0 | 2.54852 |
| 15 | 2.50986 |
| 30 | 2.47133 |

Linear interpolation of these data yield 2.4970 ± 0.0001 and 2.4842 ± 0.0001 g cm⁻³ for 20° and 25°C respectively. TRC has also recommended the above values at 20° and 25°C.

In order to represent the data as a function of temperature up to 100°C, the above data along with those of Friend and Hargreaves, and Griffing, et.al. were regressed to polynomials. Because of their higher accuracy, Timmermans data were weighted five times. However, the results were not satisfactory (av. dev. = ± 0.0012).

Subsequently the data set was subdivided into the Friend and Hargreaves subset and Griffing, et.al. subset. Because of their inherent reliability, Timmermans' values, still weighted, were retained in both subsets. There, however, resulted no improvement in correlation (av dev = ± 0.0012). It appears that the regressed data are mutually inconsistent. Our final reported results are based on a non-weighted regression of all three sets of measurements. The average error of 0.0003 g cm⁻³ is acceptable. At 15°C, the calculated density of 2.5099 g cm⁻³ is in good agreement with Timmermans' value of 2.50986 g cm⁻³. Likewise the values at 20° and 25°C are in consonance with those reported by TRC:

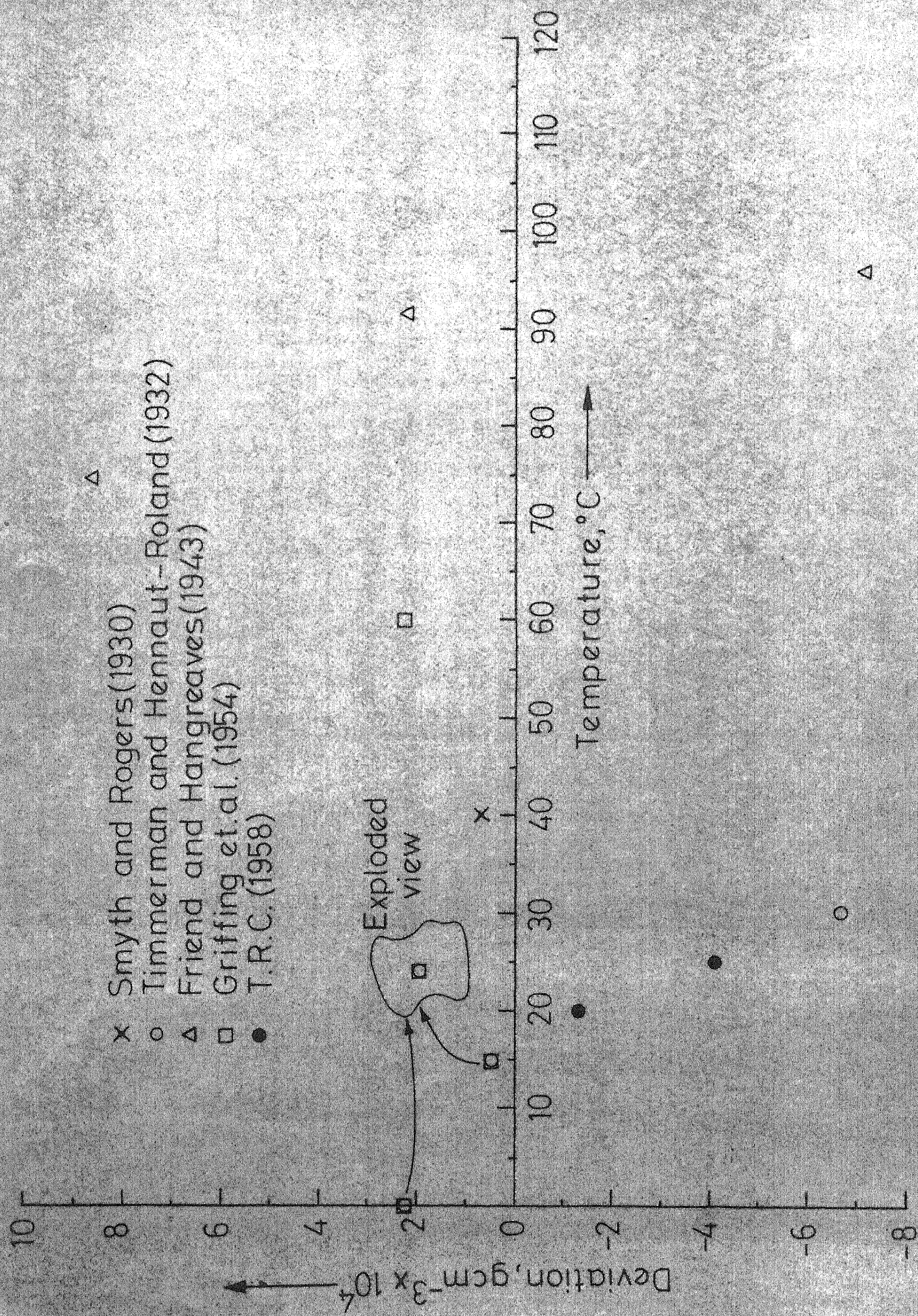


Fig. 16 - Deviation Plot for Dibromomethane(L).

| | <u>Calculated</u> | <u>TRC</u> |
|----------------------|-------------------|------------|
| $d^{20}, g\ cm^{-3}$ | 2.4969 | 2.4970 |
| $d^{25}, g\ cm^{-3}$ | 2.4838 | 2.4842 |

The figures quoted pertain to the quadratic equation, and the computed constants are recommended for predicting values from 30° to 400°C with an uncertainty of $\pm 0.0005\ gcm^{-3}$. As stated before Timmermans values are recommended from 0° to 30°C with linear interpolation to calculate the values within this range.

TRIBROMOMETHANE (CHBr₃)

Saturated liquid densities are totally absent from the published literature. For liquid density Timmermans and coworkers (1926) presented following values:

| <u>t, °C</u> | <u>d, g cm⁻³</u> |
|--------------|-----------------------------|
| 15 | 2.90350 |
| 30 | 2.86460 |

Sherman and Sherman published accurate data from 9° to 50°C using a pycnometer and a carefully purified sample. They represented their data in the following manner:

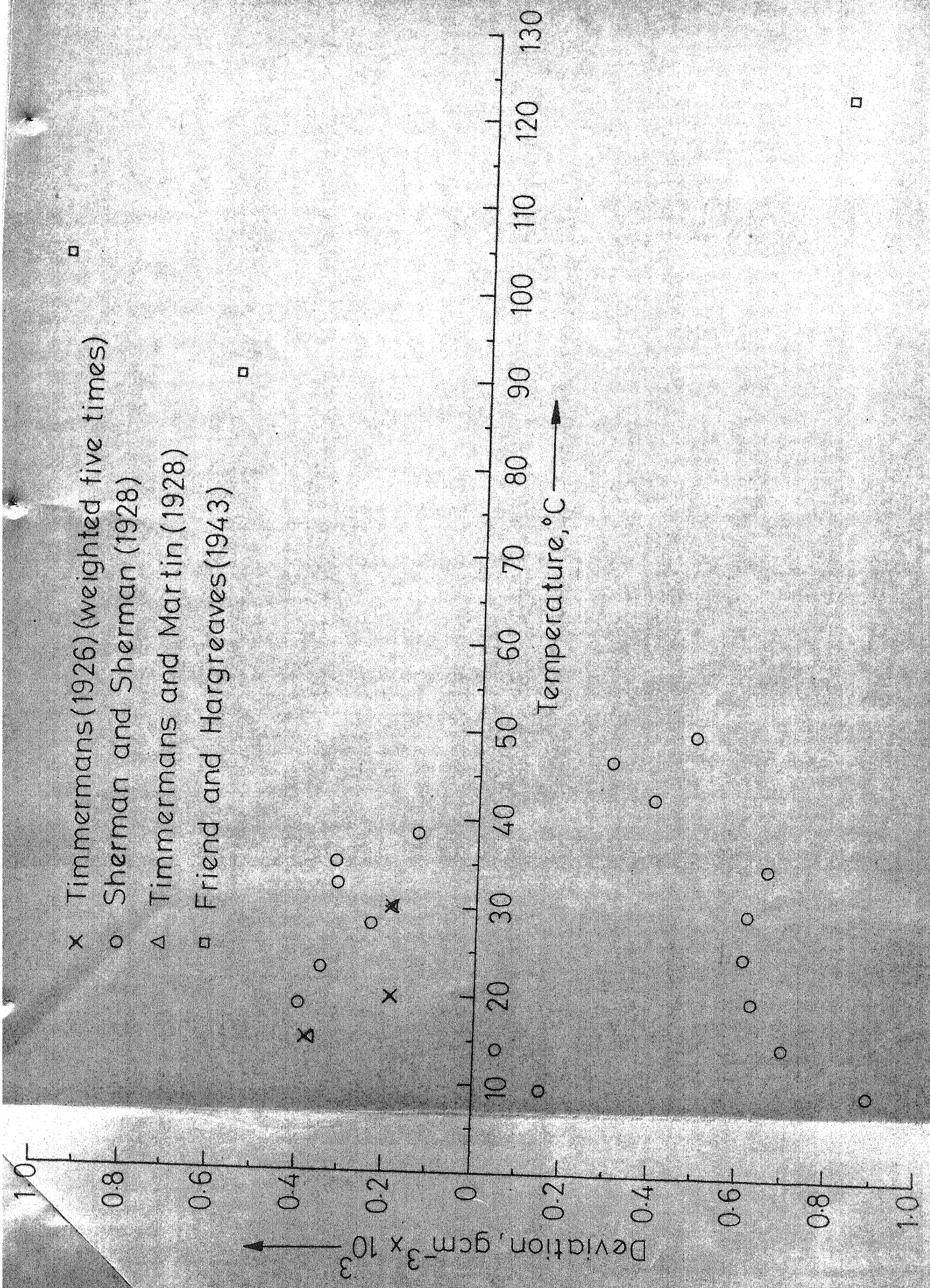
$$v_t = 0.24204 + 0.90411 \times 10^{-3}(t-7.7) + 0.6766 \times 10^{-6}(t-7.7)^2$$

In the intervening period till the work of Friend and

Hargreaves (1943), several single point values have been published, presumably with the main intention of sample identification. Not unexpectedly, therefore, most of these measurements have been at standard temperatures such as 20°C and 30°C. Friend and Hargreaves covered a higher temperature range, from 16.3° to 47.7°C, through specific gravity measurements on a distilled sample. Lagemann, et. al. (1949) also report accurate pycnometric data from 20° to 50°C, but at 10° intervals.

The data of Timmermans were selected as the most accurate. Linear interpolation of these data yielded 2.8905 and 2.8776 g cm⁻³ for 20° and 25°C respectively. In order to cover a wider range of temperature, the data of Sherman and Sherman, Friend and Hargreaves, and Lagemann were selected. The regression results for both quadratic and cubic fit were not satisfactory indicating non compatibility of these different sets of values. In spite of weighting Timmermans data five times, the deviations in these values ranged from 0.0002 to 0.0004. Various adjustments were made but the results could not be improved to match Timmermans values. Finally, the quadratic model was chosen which gave an average deviation of $\pm 0.0004 \text{ g cm}^{-3}$. The calculated densities are compared below.

| t, °C | <u>d, g cm⁻³</u> | | <u>TRC</u> |
|-------|-----------------------------|-------------------|------------|
| | <u>Present</u> | <u>Timmermans</u> | |
| 15 | 2.9039 | 2.9035 | - |
| 20 | 2.8909 | (2.8905) | 2.8889 |
| 25 | 2.8779 | (2.8776) | 2.8758 |
| 30 | 2.8648 | 2.8646 | - |



The agreement with the TRC values is not satisfactory. Hence Timmermans values are recommended at 15° and 30°C and the interpolated values (shown in parenthesis above) at 20° and 25°C. For other temperatures up to about 150°C, the above quadratic model is recommended with an uncertainty of $\pm 0.0005 \text{ g cm}^{-3}$ in the calculated value.

TETRABROMOMETHANE (CBr₄)

As early as 1943, Friend and Hargreaves published high temperature (100.7° to 190.0°C) density data for the liquid in air. Their values are based on specific gravity measurements on a distilled sample. No later data are available, except for a single density value of 2.9609 g cm^{-3} at 100°C, reported by Utermarke and Schicke in 1963. Therefore Friend and Hargreaves' data were selected and then regressed to the polynomial models, but no satisfactory correlation was possible. Even so, the cubic equation may be used, with an accuracy of ± 0.001 . The density-temperature plot is shown in Fig. 18. It is seen that the data do follow a systematic trend. Apparently, experimental inaccuracies have inhibited better correlation. There are no saturated liquid density data in the literature.

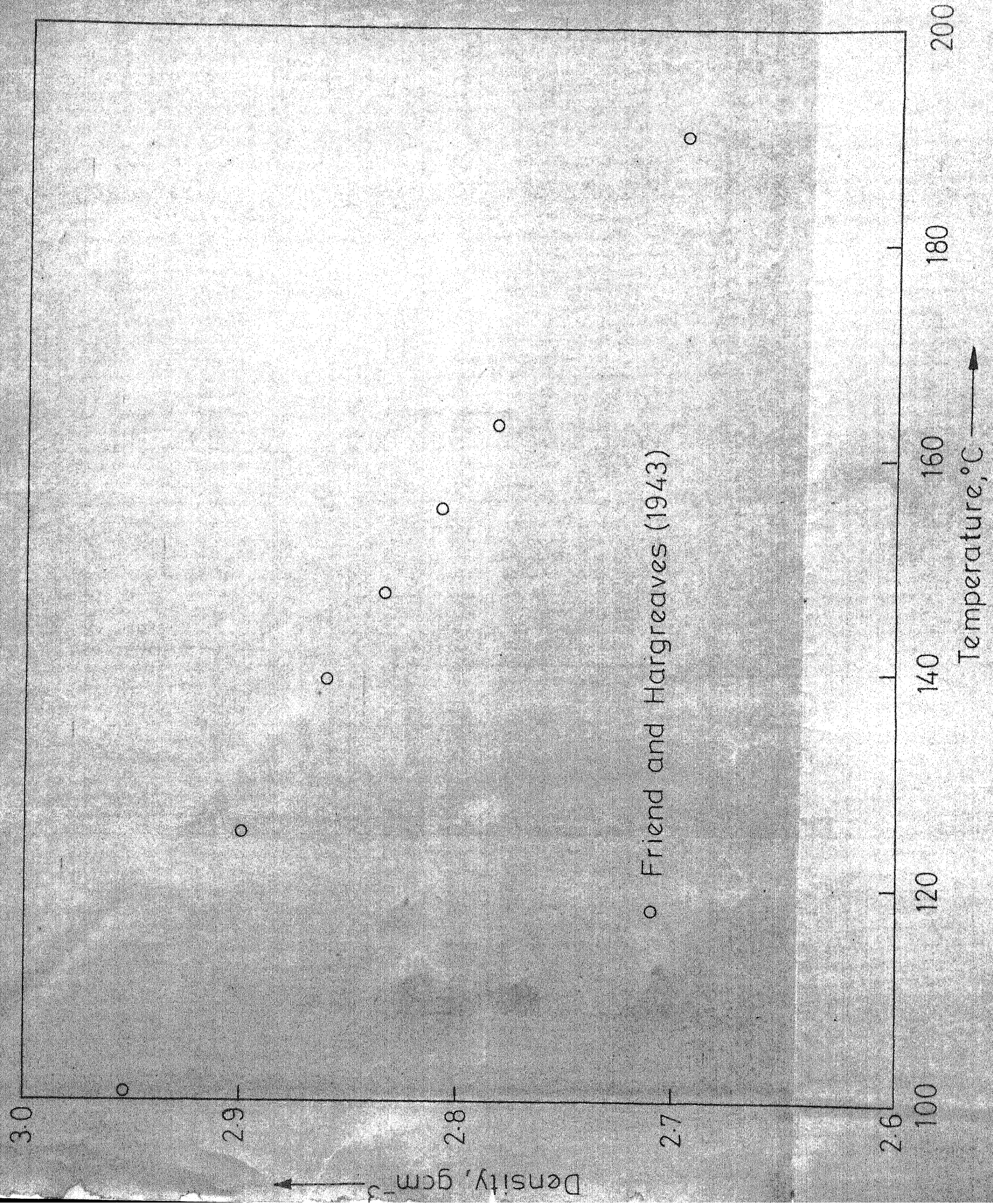


Fig.18 - Density - Temperature Plot for Tetrabromomethane(1)

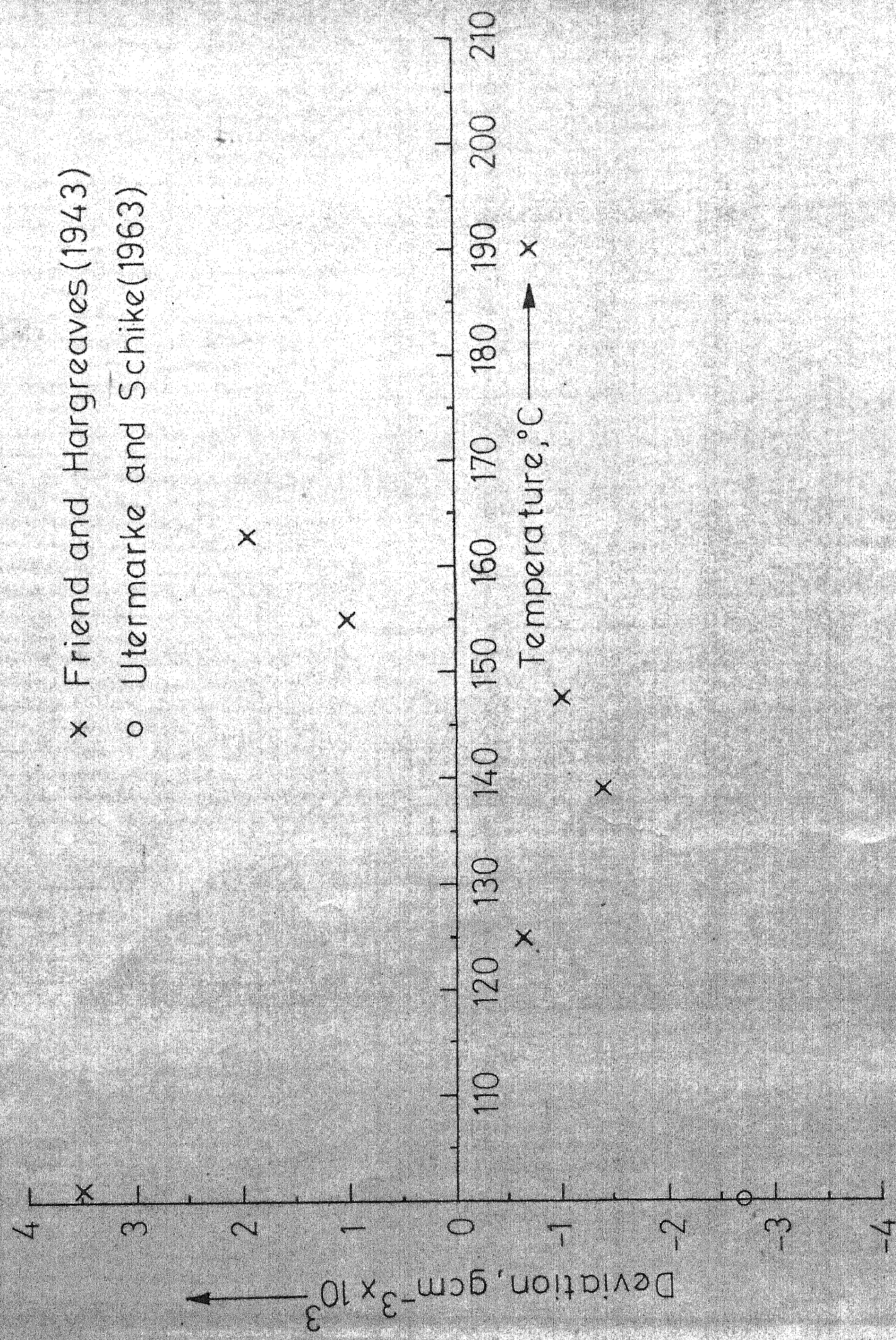


Fig 19 - Deviation Plot for Tetrabromomethane (L).

IODOMETHANE (CH₃I)

The earliest liquid densities are from Timmermans and Delcourt (1934) at 0°, 15° and 30°C. Vogel, in 1943 reported two sets of density values, for different commercial samples, using the pycnometric method. This method has also been employed by Nodiff, et.al. (1953) at 42.50°C and by Moelwyn-Hughes and Missen (1957) at 25.0°C. Bowden and Jones (1948) report a density of 2.2146 g cm⁻³ at the normal boiling point. Saturated liquid densities are available from only Morgan and Lowry (1930). Their data span the temperature range -70° to +40°C. As in several earlier compounds, the reported values have been interpolated at 10° intervals. These are the only data available and are selected.

Owing to the limited range (0° to 30°C) of liquid density data available, Timmermans values at 0°, 15°, and 30°C were selected as the best available so far.

| <u>t, °C</u> | <u>d, g cm⁻³</u> |
|--------------|-----------------------------|
| 0 | 2.33504 |
| 15 | 2.29300 |
| 30 | 2.25102 |

Linear interpolation of these data yield 2.2790 g cm⁻³ for 20°C and 2.2650 g cm⁻³ for 25°C. The former is in very good agreement with 2.2790 g cm⁻³ from Weissberger, et.al. (1958) and 2.2789 g cm⁻³ from TRC (1964). The TRC value of

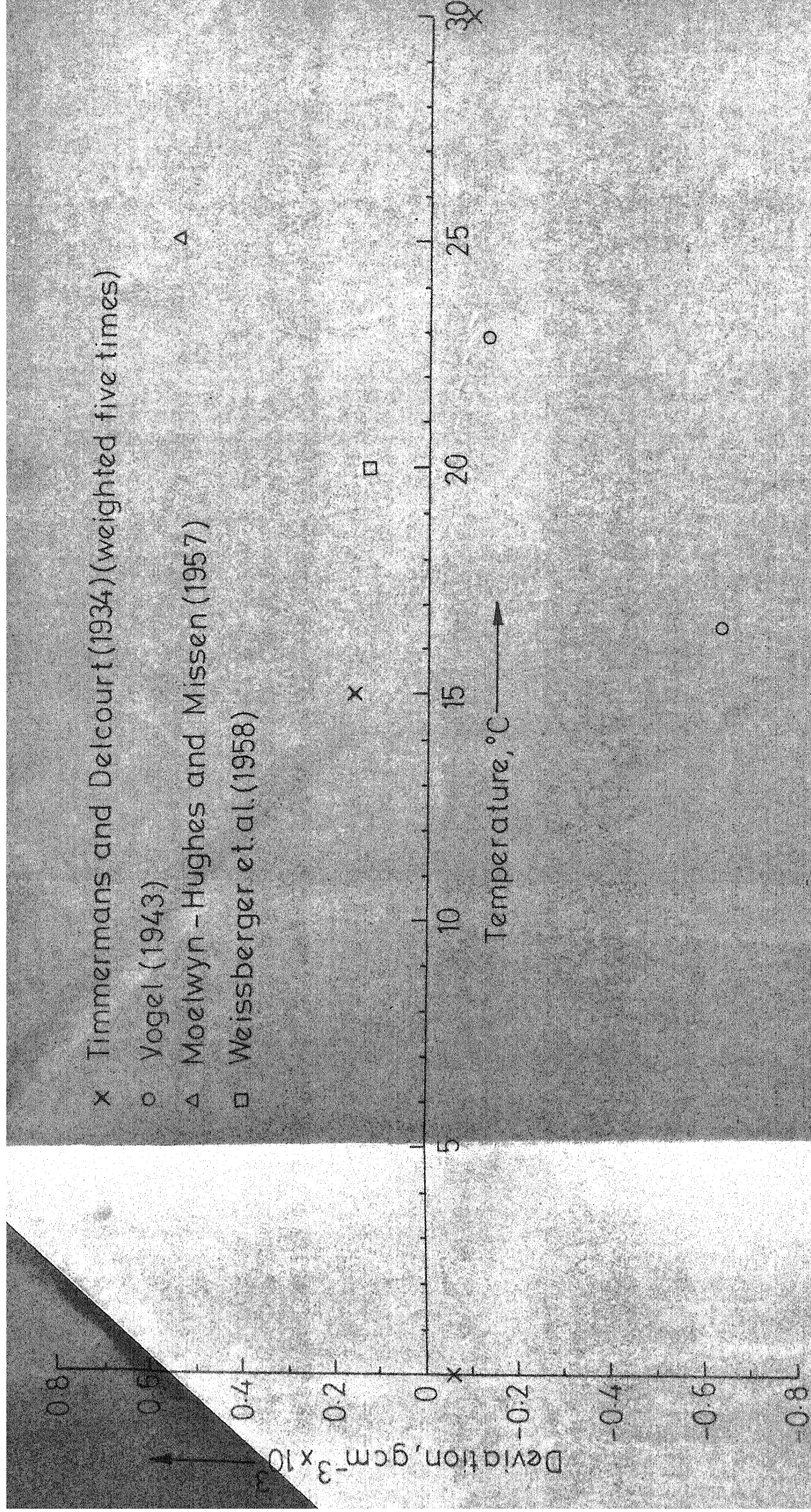
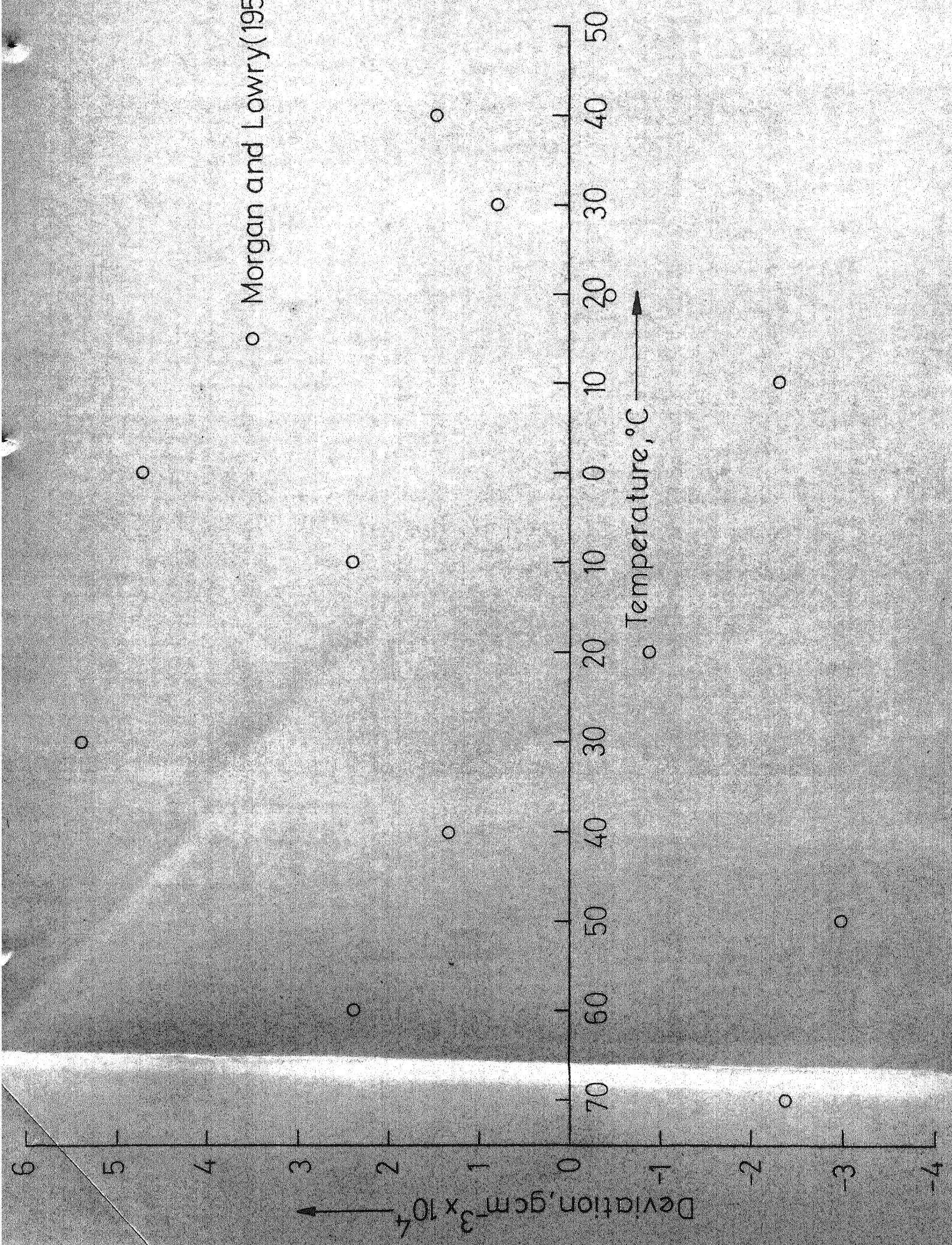


Fig.20- Deviation Plot for Iodomethane(L).

○ Morgan and Lowry(1950)



2.2649 g cm⁻³ at 25°C also agrees well.

Morgan and Lowry's data for the saturated liquid are adequately represented by a quadratic model; average error = 0.0002 g cm⁻³. However, the deviations are all positive. Hence the cubic is recommended because the deviations are random. This model is recommended for the temperature range -70° to +40°C assigning an uncertainty of ± 0.0005 units in the calculated value.

DIIODOMETHANE (CH₂I₂)

No saturated liquid density data are available. For the liquid, Smyth and Rogers (1930) report 3.3105 g cm⁻³ at 25°C from the pycnometric measurements, while from the later work of Griffing (1954) a value of 3.3073 g cm⁻³ is available at the same temperature. Timmermans (1932) has again provided accurate data as follows:

| <u>t, °C</u> | <u>d, g cm⁻³</u> |
|--------------|-----------------------------|
| 15 | 3.3345 |
| 20 | 3.3212 |
| 30 | 3.2944 |

Griffing used the balance method for a 98 mole% pure sample and reported four-decimal densities from 12.2° to 120°C. Pycnometric data are also available from Gizeskowiak, et.al. (1960) from 20° to 85°C (four data points). The lower temperature values differ from Timmermans values

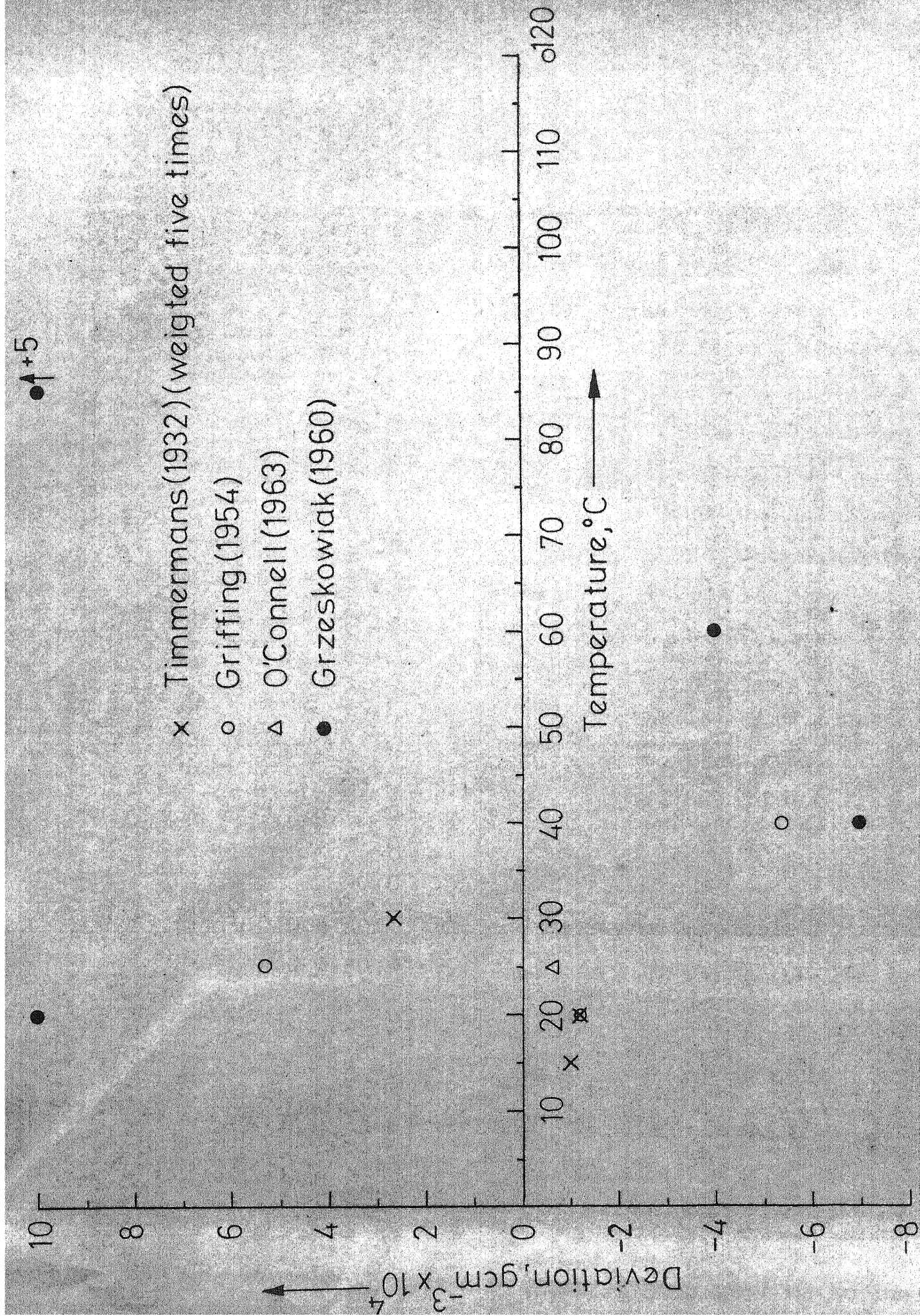


Fig. 22- Deviation Plot of Diiodomethane (L).

and hence do not seem to be accurate enough for final selection. The values of Timmermans, and of Griffing were selected. For the regression, Timmermans values were weighted five times as before. The regression indicated that Timmermans data and that of Griffing were not quite compatible. Since the latter yielded larger errors and also because Timmermans' data are more reliable, certain values of Griffing were rejected, primarily in the lower temperature range, which was still covered by Timmermans. This is a feature of all rejections for any compound; as far as possible it was ensured that rejection of a set of points did not introduce a large "temperature gap" where no data points were present. The quadratic model is recommended with an uncertainty of ± 0.0005 in the calculated value. At 20°C and 25°C , the calculated densities of 3.3211 and 3.3078 g cm^{-3} are identical with those of TRC (1961).

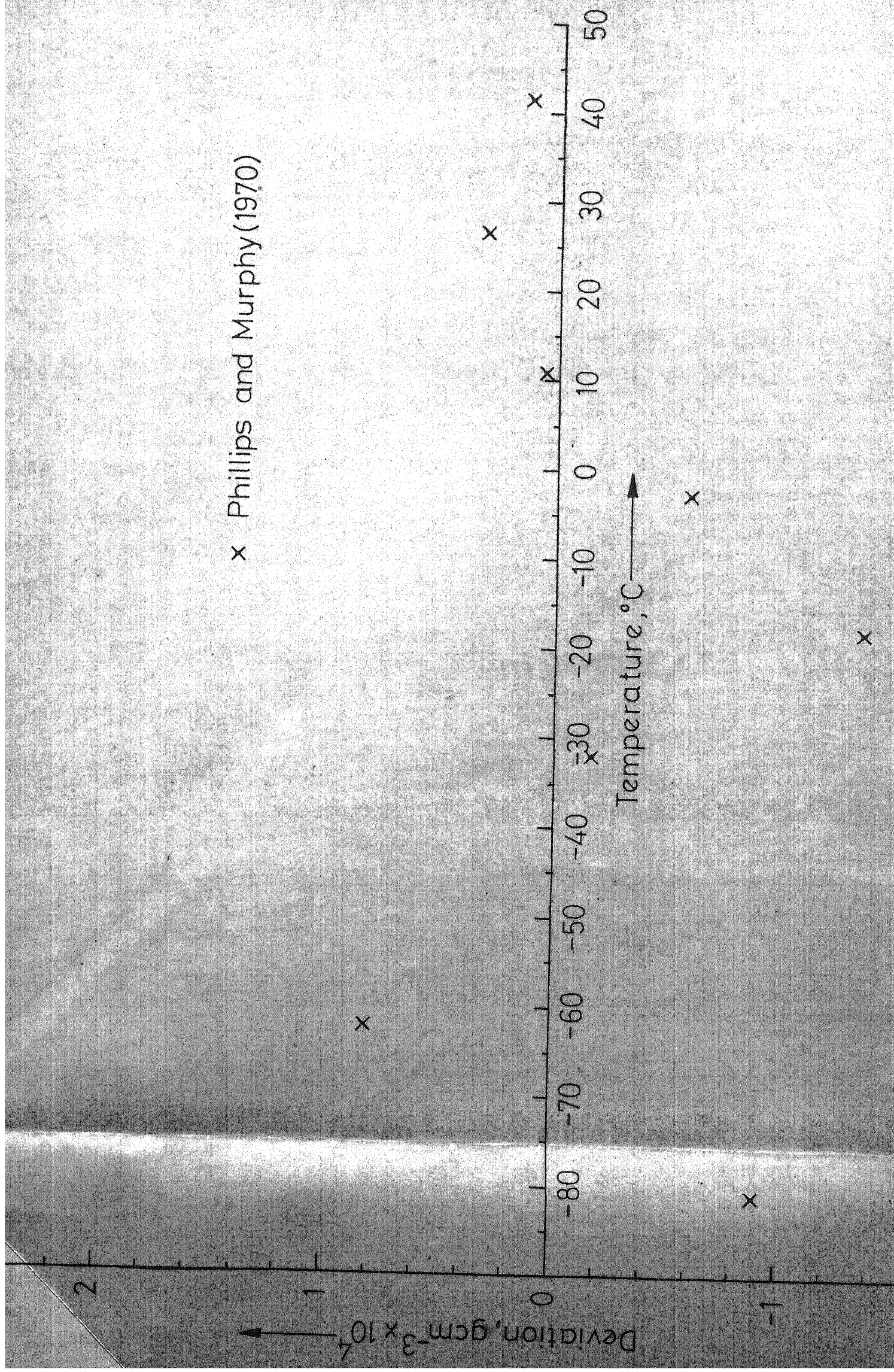
TRIIODOMETHANE (CHI_3) AND TETRAIODOMETHANE (CI_4)

No data for liquid or saturated liquid densities are available.

FLUOROCHLOROMETHANE (CH_3FCl)

Only Phillips and Murphy (1970) have reported density data and pertain to the saturated liquid. For a 99.90 mole% pure sample, their nine data points span the range -80.95° to

x Phillips and Murphy (1970)



+41.40°C. These are the only reliable data available and hence are selected. Polynomial regressions favor the cubic model, which represents density behavior over the regressed temperature range with an average error of $0.00008 \text{ g cm}^{-3}$. While this is admittedly indicative of a very good correlation Phillips and Murphy's value of 1.3924 g cm^{-3} at -62.22°C appears suspect in that it is away from the trend of the other values and was therefore removed (dev. of 0.0012 in quadratic and 0.0003 g cm^{-3} in the cubic models for this value). The cubic model is recommended for calculations between -80° to 50°C and an accuracy of $\pm 0.0002 \text{ g cm}^{-3}$ is assigned to the calculated value.

FLUOROIODOMETHANE (CH_2FI), CHLOROBROMOMETHANE (CH_2ClBr),

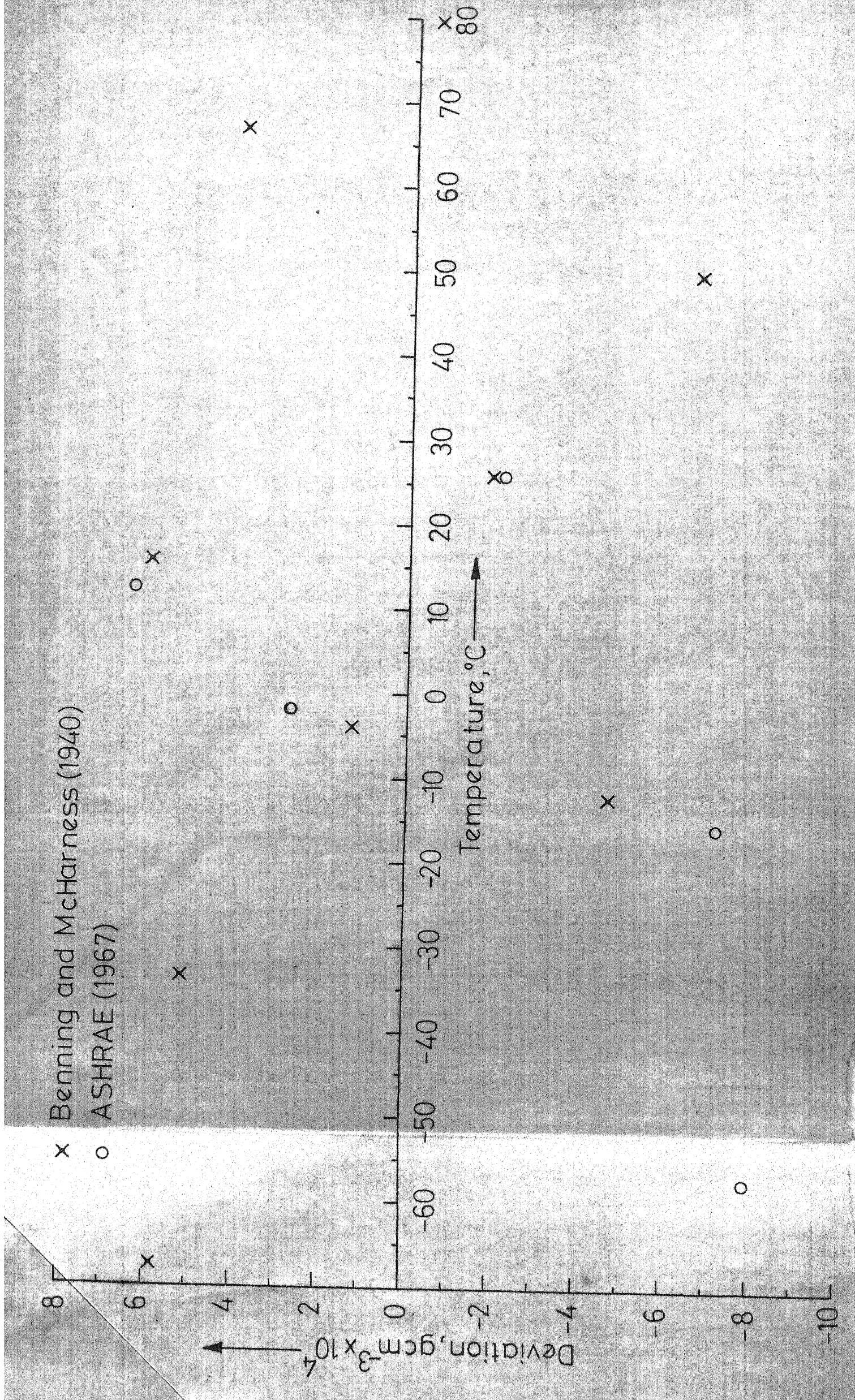
CHLOROIODOMETHANE (CH_2ClI)

Altogether only five data points are available for these compounds. For CH_2FI ^{barring} a single value at 20°C reported by Van Arbel and Janetzby in 1937, all values are from Stevels (1937). Owing to dearth of "good" data, the following values are recommended as approximate.

| <u>Compound</u> | <u>t, °C</u> | <u>d, g cm⁻³</u> |
|--------------------------|--------------|-----------------------------|
| CH_2FI | 20 | 2.366 ± 0.001 |
| CH_2ClBr | 20 | 1.940 ± 0.001 |
| CH_2ClI | 20 | 2.422 ± 0.001 |

x Benning and McHarness (1940)

o ASHRAE (1967)



DIFLUOROCHLOROMETHANE (CHF_2Cl):

Benning and McHarness (1940) have reported density data for the saturated liquid in the temperature range -69° to $+87^\circ\text{C}$, measurements being made by dilatometer. ASHRAE (1967) have reported density values for the saturated liquid (99.90 mole % pure) from -72° to $+25^\circ\text{C}$. Neither of these two groups have mentioned the accuracy of the measurements. Data for liquid in air are not available. Both sets of data for the saturated liquid were selected. These were regressed and fit the Martin equation with an average error of $\pm 0.0004 \text{ g cm}^{-3}$. The Martin model is recommended for the temperature range -75 to $+90^\circ\text{C}$ and an uncertainty of $\pm 0.0005 \text{ g cm}^{-3}$ is assigned to the calculated value.

DIFLUOROBROMOMETHANE (CHF_2Br) AND DIFLUOIODOMETHANE(CHF_2I)

No data for the liquid or saturated liquid densities are available.

FLUORODICHLOROMETHANE (CHFCl_2)

For the saturated liquid two sets of data are available. Benning and McHarness (1940) have measured, by dilatometric method, saturated liquid densities between -40° and $+169^\circ\text{C}$. Later data from ASHRAE (1967) cover a smaller temperature region (-65° to 74°C) for a 99.90 mole% pure sample. These

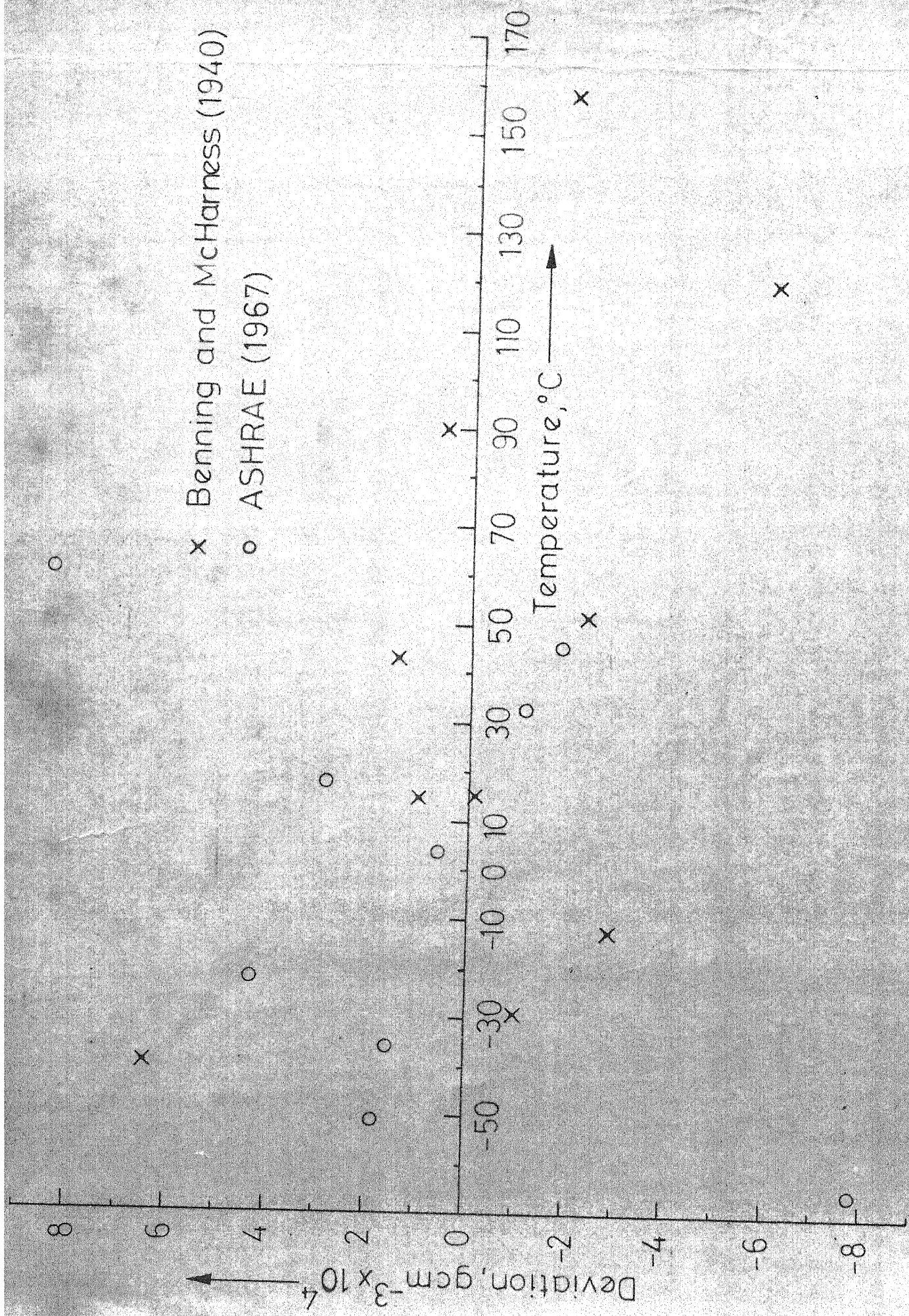


Fig. 25- Deviation Plot for Fluorodichloromethane (SL).

data are selected and were processed further. The Martin equation represents both sets of data very well (average error = $\pm 0.0003 \text{ g cm}^{-3}$) and is recommended for the saturated liquid from -60 to $+170^\circ\text{C}$ assigning an accuracy of $\pm 0.0005 \text{ g cm}^{-3}$ in the calculated value.

FLUORODIBROMOMETHANE (CHBr_2) AND FLUORODIIODOMETHANE (CHI_2)

The available data are scanty, very old (1910 to 1937) and unreliable. For CHBr_2 , Swarts reports 2.4256 g cm^{-3} at 18.5°C and Stevels, 2.421 at 20°C . For 20°C , $2.421 \pm 0.0001 \text{ g cm}^{-3}$ is recommended.

For CHI_2 , Ruff, et.al. (1936) reports the following three values:

| <u>t, °C</u> | <u>d, g cm⁻³</u> |
|--------------|-----------------------------|
| -19.4 | 3.3313 |
| +14.4 | 3.2206 |
| 21.5 | 3.1969 |

The interpolated value of $3.202 \pm 0.0001 \text{ g cm}^{-3}$ at 20°C is recommended.

DICHLOROBROMOMETHANE (CHCl_2Br)

Timmermans and Martin (1926) have reported three density values at 0°, 15° and 30°C. An intermediate value at 20°C has been reported by Stevels (1937). Because of their reliability, Timmermans and Martin's data are selected and recommended.

| <u>t, °C</u> | <u>d, g cm⁻³</u> |
|--------------|-----------------------------|
| 0 | 2.0385 |
| 15 | 2.0055 |
| 30 | 1.9724 |

Linear interpolation yields 1.9945 and 1.9835 g cm⁻³ at 20°C and 25°C. These values are recommended with an uncertainty of ± 0.0001 in all values.

DICHLOROIODOMETHANE (CHCl_2I)

Stevels (1937) reports 2.392 at 20°C and Hine and Cowell (1954) report 2.3853 at 25°C. The following values are recommended.

| <u>t, °C</u> | <u>d, g cm⁻³</u> |
|--------------|-----------------------------|
| 20 | 2.392 \pm 0.001 |
| 25 | 2.385 \pm 0.001 |

CHLORODIBROMOMETHANE (CHClBr₂)

Stevens has reported 2.451 g cm^{-3} at 20°C and a value of 2.411 at 32°C by Hine et. al. (1956). Stevens's value is selected assigning an uncertainty of ± 0.001 in this value.

CHLORODIODOMETHANE (CHClI₂)

Only, a single value of 3.17 at 0°C is reported by Auger (1907). Hence no selection.

TRIFLUOROCHLOROMETHANE (CF₃Cl)

For the liquid state just two pycnometric values (at -130°C and -82°C) are available, from Ruff and Keim(1931). Data for the saturated liquid have been reported by Riedel (1941) (1941) and by Albright and Martin (1952). Riedel's values cover the range -140° to $+25.10^\circ\text{C}$, but lack experimental details. More detailed information has been furnished by Albright and Martin, whose float technique measurements on a 99.9 mole % pure sample yielded accurate and reliable data from -142.25° to $+25.60^\circ\text{C}$. Consequently, we have selected the data of Albright and Martin only. Moreover, this choice is justified also by the observation that the selected set fully covers the range of Riedel's data. Regression to the Martin equation was satisfactory, with an average error of $\pm 0.0003 \text{ g cm}^{-3}$. Hence the Martin model is recommended for the temperature range -140° to $+80^\circ\text{C}$ with an uncertainty

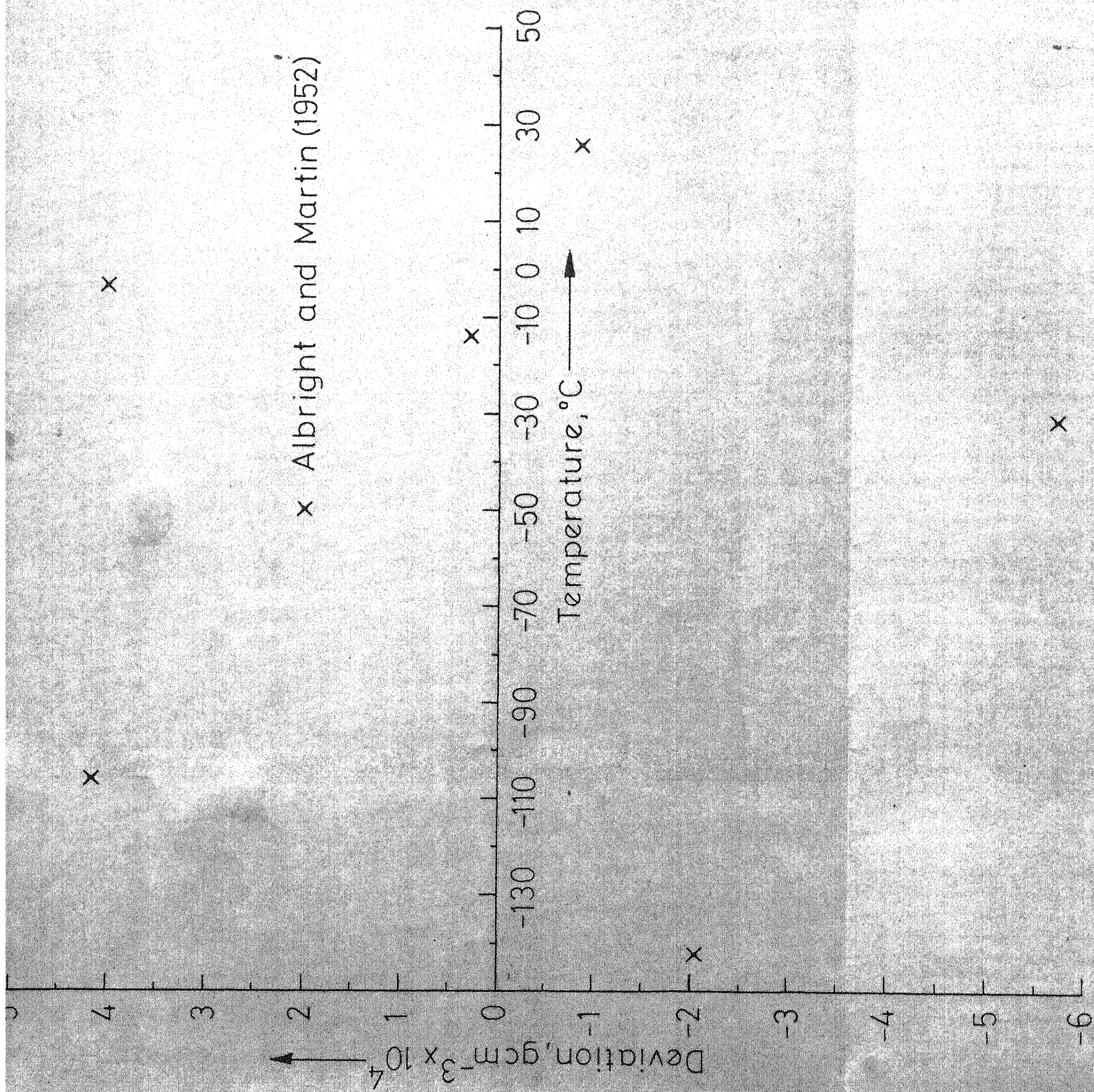


Fig.26- Deviation Plot for Trifluorochloromethane (SL).

of ± 0.0015 is the calculated value.

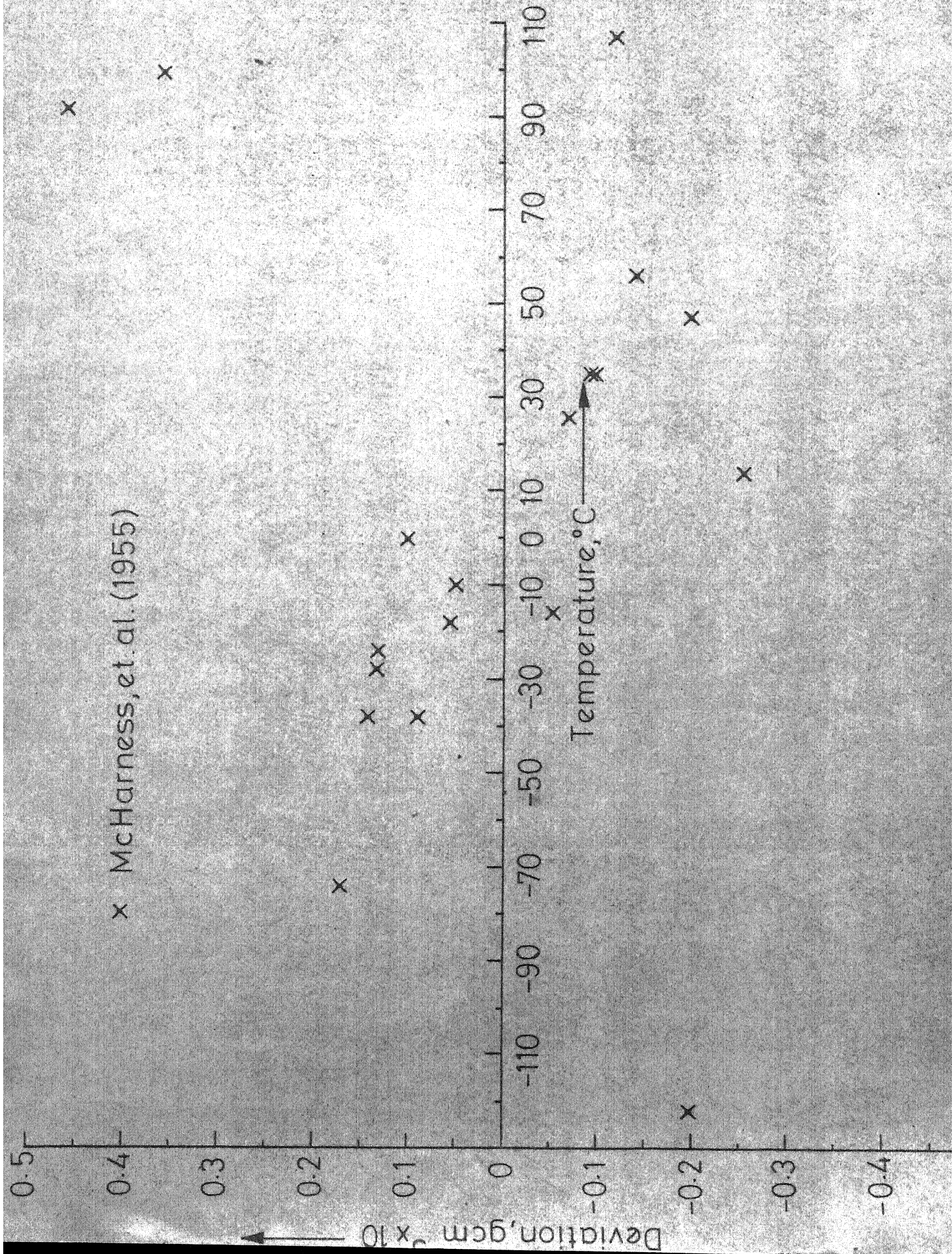
TRIFLUOROBROMOMETHANE (CF_3Br) and TRIFLUOROiodo-
METHANE (CF_3I)

Only saturated liquid data are available for the first compound and only liquid density values for the second. In neither case are they complete enough to permit evaluation.

| <u>CF_3Br (SL)</u> | | | <u>CF_3I (L)</u> | | |
|---|-----------------------------|--------------------------|---|-----------------------------|--------------------------|
| <u>t, °C</u> | <u>d, g cm⁻³</u> | <u>Author</u> | <u>t, °C</u> | <u>d, g cm⁻³</u> | <u>Author</u> |
| -59 | 1.96 | | -78.5 | 2.548 | |
| -54 | 1.94 | Nodiff, et. al (1953) | -32.5 | 2.361 | Nodiff, et. al (1953) |
| -18 | 1.78 | | | | |

DIFLUORODICHLOROMETHANE (CF_2Cl_2)

Only Ruff and Keim (1931) have reported three values of liquid densities, at -114.8° , -84.8° , and -72.8°C , which however, are too few to be analyzed. Saturated liquid data are available from Bichowsky and Gilkey (1931), between -40° and $+110^\circ\text{C}$, Vaziri (1943), in the range of $+55^\circ$ to $+110^\circ\text{C}$, and McHarness, et.al. (1955), who have meticulously covered the temperature range -121.91° to $+112.00^\circ\text{C}$ for a 99.95 mole% pure sample. McHarness, et.al. have employed both the float technique and the dilatometric method. The data of



McHarness et.al. are selected as the best available. These data were then regressed to Martin model. It should, however, be noted that the average error was still ± 0.0018 . Results at sample points are as follows:

| <u>t, °C</u> | <u>d_{cal}, g cm⁻³</u> | <u>d_{expt.}, g cm⁻³</u> |
|--------------|---|---|
| -73.71 | 1.6099 | 1.6082 |
| 0.0 | 1.3955 | 1.3945 |
| 91.1 | 0.9831 | 0.9785 |

The uncertainty in the selected data is estimated to be $\pm 0.002 \text{ g cm}^{-3}$.

DIFLUORODIBROMOMETHANE (CF₂Br₂)

Only one value 2.3492 g cm^{-3} at 0°C is available from Desirant (1958). This value is recommended at 0°C with ± 0.001 uncertainty.

FLUOROTRICHLOROMETHANE (CFCl₃)

Data for the liquid density are very sparse. Ruff and Keim (1931) reported a few values between -130.15°C and -72.15°C . Desereux (1935), Stevels (1937) and Pavlova (1958) have reported single density values. None of these authors have either furnished experimental details nor done measurements extensive and accurate enough to justify selection. For

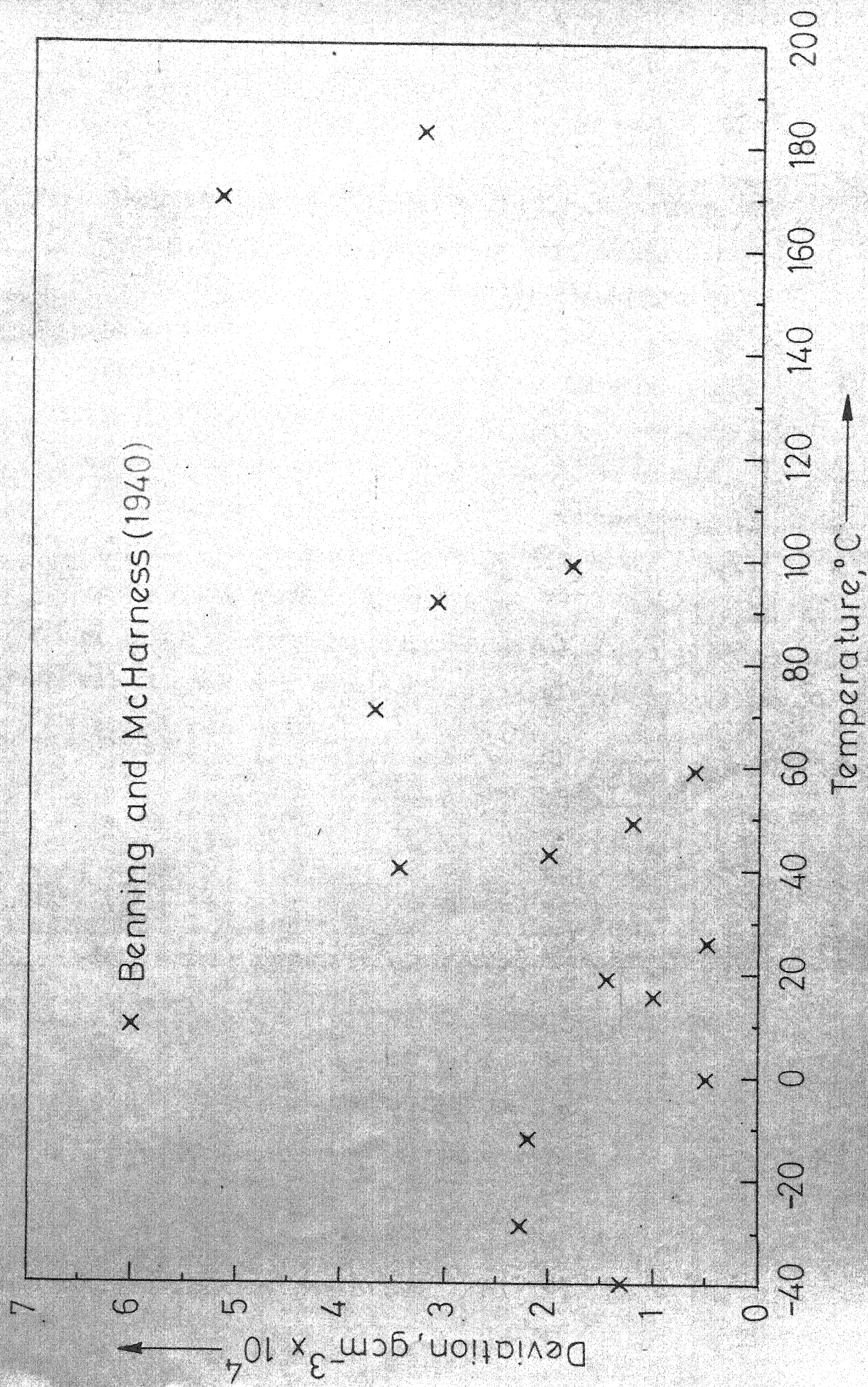


Fig. 28- Deviation Plot for Fluorotrichloromethane (SL)

the saturated liquid, Benning and McHarness (1940) have extensively covered the temperature region from -40° to $+191^{\circ}\text{C}$ by dilatometric measurements. Theirs is the only set of data available and was selected and regressed quite satisfactorily to the Martin equation (maximum error = 0.0002 g cm^{-3}). While our computed Martin constants are recommended, users are cautioned that all deviations in the final regression were positive. The recommended regression excludes their values at 120.68° and 152.80°C , as these yielded large deviations ($\pm 0.010 \text{ g cm}^{-3}$). Even though the errors later were not randomly scattered, the improvement in overall fit has been substantial. Results for three sample points are shown below:

| <u>t, °C</u> | <u>d_{calc.}, g cm⁻³</u> | <u>d_{expt.}, g cm⁻³</u> |
|--------------|---|---|
| -29.20 | 1.5992 | 1.5990 |
| 26.10 | 1.4733 | 1.4733 |
| 98.89 | 1.2793 | 1.2791 |

The uncertainty in the estimated value is estimated to be $\pm 0.0005 \text{ g cm}^{-3}$.

FLUOROTRIBROMOMETHANE (CFBr₃)

For the liquid, the following values are available:

| <u>t, °C</u> | <u>d, g cm⁻³</u> | <u>Author</u> |
|--------------|-----------------------------|-----------------|
| 20 | 2.7648 | Desreux (1935) |
| 20 | 2.757 | Stevens (1937) |
| 0 | 2.8211 | Desirant (1958) |
| 20 | 2.7648 | Desirant (1958) |

The values of Desirant truncated to 3 decimal places are recommended assigning an uncertainty of $\pm 0.001 \text{ g cm}^{-3}$ in each value.

TRICHLOROBROMOMETHANE (CCl₃Br)

The following values for the liquid density are available.

| <u>t, °C</u> | <u>d, g cm⁻³</u> | <u>Author</u> |
|--------------|-----------------------------|------------------|
| 20 | 2.012 | Stevens (1937) |
| 20 | 1.9942 | Zokhorkin (1952) |

For 20°C, $2.00 \pm 0.01 \text{ g cm}^{-3}$ is recommended.

TRICHLOROIODOMETHANE (CCl₃I)

Stevens has reported a single value of 2.355 g cm^{-3} at 20°C for the liquid. This is the only value and is recommended assigning an uncertainty of $\pm 0.005 \text{ g cm}^{-3}$.

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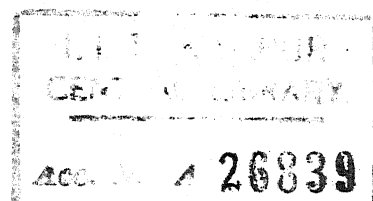
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TABLE 1.: STATUS OF DENSITY DATA FOR HALOMETHANES

Symbols: A = Adequate and good experimental data available up to the critical point.

A* = Adequate and good experimental data available up to the boiling point

B = Inadequate and scanty data (needs further experimentation).

Note: Data from the underlined references are the selected data. References in parentheses contain data for the saturated liquid.

| Sl.No. | Compound | Status | References | Equation(s) recommended |
|--------|---------------------------------|--------|---|-------------------------|
| 1. | CH ₃ F | B | (28), (59) | (1) |
| 2. | CH ₂ F ₂ | A* | 99 | 2 |
| 3. | CHF ₃ | A | 3, (73) | (3) |
| 4. | CF ₄ | A* | (1), 83, (84), (85), 138, 140, 141 | (1) |
| 5. | CH ₃ Cl | A | 20, (31), (32), (72), (75), 113, 122, (138), (157), 174, 195 | 1, (3) |
| 6. | CH ₂ Cl ₂ | A* | 9, 20, 36, (45), 46, 56, 57, 91, 97, 106, 109, 113, 114, 117, 118, (130), 154, 163, 174 | 1, (2) |
| 7. | CHCl ₃ | A | 4, 19, 20, 21, 23, (26), 28, 33, 34, 36, 42, 53, 56, (66), 68, 71, 81, 86, 92, 103, 109, 113, 118, (130), 132, 138, 154, 158, 159, 160, 165, 167, 169, 170, 172, 173, 174, 181, 189, 195, 198 | 1, (3) |
| 8. | CCl ₄ | A | 4, 7, 10, 17, 19, 20, 21, 22, 23, (27), 33, 35, 37, 39, 40, 41, 42, 48, 50, 52, 55, 56, 58, 62, 63, 67, 68, 76, 78, 79, 80, 82, 86, (87), 89, 92, 94, 103, 104, 106, 107, 109, 111, 112, 113, | 1, (3) |

Table 1 (continued)

| Sh. No. | Compound | Status | References | Equation(s) recommended |
|---------|--------------------------|--------|---|-------------------------|
| | CCl_4 | | 115, 117, 118, 119, 120, 123, 124, 127, (131), (132), 134, 144, 145, 146, 150, 151, 154, 165, 168, 170, 172, 173, 174, 175, 177, 184, 185, 186, 190, 191, 193, (193), (196), (197), 199 / | |
| 9. | CH_3Br | A* | (74), (113), 122, 174 | (1) |
| 10. | CH_2Br_2 | A* | 16, 44, 51, 57, 88, 92, 97, 114, 125, 152, 154, 163, 174 | 1 |
| 11. | CHBr_3 | A* | 4, 7, 25, 39, 49, 50, 51, 64, 92, 98, 125, 126, 149, 152, 154, 164, 166, 167, 168, 173, 174, 188, 189, 191 | 1 |
| 12. | CBr_4 | B | 51, 173 | 2 |
| 13. | CH_3I | A* | 5, 20, 60, 109, (113), 114, 154, 162, 174, 178, 180, 186, 195, 197 | 1, (2) |
| 14. | CH_2I_2 | A* | 57, 61, 64, 91, 97, 114, 125, 129, 152, 154, 161, 173, 174 | 1 |
| 15. | CHI_3 | - | Data are available for solid state only | - |
| 16. | CHI_4 | - | Data are available for solid state only | - |
| 17. | CH_2FCl | A* | (130) | (2) |
| 18. | CH_2FBr | - | No data are available | - |
| 19. | CH_2FI | B | 154, 175 | - |
| 20. | CH_2ClBr | B | 154, 155 | |
| 21. | CH_2ClI | B | 154 | |
| 22. | CH_2BrI | - | No data are available | - |
| 23. | CHF_2Cl | A | (13), (130) | (3) |

Table 1 (continued)

| Sl.No. | Compound | Status | References | Equation(s) recommended |
|--------|--------------------------|--------|---|----------------------------|
| 24. | CHF_2Br | - | Data are available for saturated vapor only | - |
| 25. | CHF_2I | - | Data are available for solid state only | - |
| 26. | CHFCl_2 | A | (3), (13), 154 | (3) |
| 27. | CHFClBr | - | No data are available | - |
| 28. | CHFClI | - | No data are available | - |
| 29. | CHFBr_2 | B | 154, 156 | - |
| 30. | CHFBrI | - | No data are available | - |
| 31. | CHF_2 | B | 143 | - |
| 32. | CHCl_2Br | B | 154, 164 | - |
| 33. | CHCl_2I | B | 6, 24, 69, 154 | - |
| 34. | CHClBr_2 | B | 70, 154 | - |
| 35. | CHClBrI | - | No data are available | - |
| 36. | CHClI_2 | B | 6 | - |
| 37. | CHBr_2I | - | No data are available | - |
| 38. | CHBrI_2 | - | No data are available | - |
| 39. | CF_2Cl | A | (2), (136), 141 | (3) |
| 40. | CF_3Br | B | (121), (122), (182) | - |
| 41. | CF_3I | B | 8, 122 | - |
| 42. | CF_2Cl_2 | A | (15), 195, 116, 141, (177) | (3) |
| 43. | CF_2ClBr | - | No data are available | - |
| 44. | CF_2ClI | - | No data are available | -- |
| 45. | CF_2Br_2 | B | 37 | - |

Table 1 (continued)

| Sl.No. | Compound | Status | References | Equation(s) recommended |
|--------|---------------------------|--------|----------------------------------|----------------------------|
| 46. | CF_2BrI | - | No data are available | - |
| 47. | CF_2I_2 | - | No data are available | - |
| 48. | CFCl_3 | A | (13), (14), 39, 128, 141, 154 | (3) |
| 49. | CFCl_2Br | - | No data are available | - |
| 50. | CFCl_2I | - | No data are available | - |
| 51. | CFClBr_2 | - | No data are available | - |
| 52. | CFClBrI | - | No data are available | - |
| 53. | CFClI_2 | - | No data are available | - |
| 54. | CFBr_3 | - | 38, 39, 154 | - |
| 55. | CFBr_2I | - | No data are available | - |
| 56. | CFBrI_2 | - | No data are available | - |
| 57. | CFI_3 | - | No data are available | - |
| 58. | CCl_3Br | B | 154, 199 | - |
| 59. | CCl_3I | B | 154 | - |
| 60. | CCl_2Br_2 | - | No data are available | - |
| 61. | CCl_2BrI | - | No data are available | - |
| 62. | CCl_2I_2 | - | No data are available | - |
| 63. | CClBr_3 | - | No data are available | - |
| 64. | CClBr_2I | - | No data are available | - |
| 65. | CClBrI_2 | - | No data are available | - |
| 66. | CClI_3 | - | No data are available | - |
| 67. | CBr_3I | - | No data are available | - |
| 68. | CBr_2I_2 | - | No data are available | - |
| 69. | CBrI_3 | - | No data are available | - |

TABLE 2: SUMMARY OF REGRESSION CONSTANTS FOR THE DENSITIES OF LIQUID HALOMETHANES

Equation 1. $d = A + BT + CT^2$

2. $d = A + BT + CT^2 + DT^3$

3. $d - d_0 = A(1 - T_r)^{1/3} + B(1 - T_r)^{2/3} + C(1 - T_r) + D(1 - T_r)^{4/3}$

where d = density, gcm^{-3} ; d_c = critical density, gcm^{-3} ; (Kudchadker et.al.(90))

T = temperature, K ; T_c = critical temperature, K; (Kudchadker et.al.(90))

T_r = reduced temperature = T/T_c

N = number of data points used in the final regression

A, B, C, D = regression constants ; *Strictly for interpolation only

| Compound and State | Eqn. No. | Empirical constants | | | | Range, °C | N |
|-------------------------------------|----------|---------------------|------------------|------------------|------------------------|--------------|----|
| | | A | $-B \times 10^3$ | $-C \times 10^4$ | $-D \times 10^4$ | | |
| $\text{CH}_3\text{F}^*(\text{SL})$ | 1 | 1.2080 | 1.2884 | 0.01992 | - | -130 to -60 | 5 |
| $\text{CH}_2\text{F}_2(\text{L})$ | 2 | 3.5378 | 10.983 | -0.15554 | 0.00025 | -75 to 15 | 10 |
| $\text{CHF}_3(\text{SL})$ | 3 | 1.0265 | 3.9944 | -21.443 | 15073 | -85 to 25 | 19 |
| $\text{CF}_4(\text{SL})$ | 1 | 2.2529 | 3.6188 | 0.05474 | - | -180 to -115 | 26 |
| $\text{CH}_3\text{Cl}(\text{L})$ | 1 | 1.4997 | 2.4046 | -0.01779 | - | -90 to -20 | 8 |
| $\text{CH}_3\text{Cl}(\text{SL})$ | 3 | 0.80560 | 971.50 | -28071 | 19430 | 20 to 130 | 18 |
| $\text{CH}_2\text{Cl}_2(\text{L})$ | 1 | 1.8377 | 1.6901 | 0.001917 | - | -100 to 40 | 38 |
| $\text{CH}_2\text{Cl}_2(\text{SL})$ | 2 | 1.7822 | 1.1597 | 0.01548 | -0.65×10^{-5} | -65 to 100 | 14 |
| $\text{CHCl}_3(\text{L})$ | 1 | 2.0191 | 1.7473 | 0.002066 | - | -65 to 30 | 15 |

Table 2 (contd.)

| Sl. No. | Compound and State | Eqn. No. | Empirical Constants | | | | Range, °C | N |
|---------|-------------------------------------|----------|---------------------|------------------|------------------|-----------------------|-------------|----|
| | | | A | $-B \times 10^3$ | $-C \times 10^4$ | $-D \times 10^4$ | | |
| 10. | $\text{CHCl}_3(\text{SL})$ | 3 | 0.52808 | -2558.8 | 43863 | -39226 | 100 to 265 | 26 |
| 11.a. | $\text{CCl}_4(\text{L})$ | 1 | 2.0608 | 1.2474 | 0.01175 | - | 0 to 70 | 21 |
| 11.b. | $\text{CCl}_4(\text{L})$ | 1 | 2.0921 | 1.4595 | 0.00817 | - | 0 to 40 | 12 |
| 12 | $\text{CCl}_4(\text{SL})$ | 3 | 0.79078 | -1439.8 | 20387 | -13835 | 20 to 270 | 73 |
| 13. | $\text{CH}_3\text{Br}(\text{SL})$ | 1 | 2.3232 | 1.7037 | 0.01722 | - | -95 to 50 | 17 |
| 14. | $\text{CH}_2\text{Br}_2(\text{L})$ | 1 | 3.1840 | 2.0759 | 0.009142 | - | 0 to 100 | 12 |
| 15. | $\text{CHBr}_3(\text{L})$ | 1 | 3.5603 | 1.9668 | 0.01080 | - | 10 to 125 | 31 |
| 16. | $\text{CBr}_4(\text{L})$ | 2 | -1.9217 | -37.181 | 0.88823 | -0.000649 | 100 to 190 | 8 |
| 17. | $\text{CH}_3\text{I}(\text{L})$ | 1 | 3.0233 | 2.2660 | 0.00930 | - | 0 to 45 | 20 |
| 18. | $\text{CH}_3\text{I}(\text{SL})$ | 2 | 3.1123 | 2.9157 | -0.003958 | 0.77×10^{-5} | -70 to 40 | 12 |
| 19. | $\text{CH}_2\text{I}_2(\text{L})$ | 1 | 4.2314 | 3.5538 | -0.01531 | - | 15 to 120 | 16 |
| 20. | $\text{CH}_2\text{FCI}(\text{SL})$ | 2 | 2.0156 | 4.0559 | 0.08306 | 0.000136 | -82 to 40 | 8 |
| 21. | $\text{CHF}_2\text{Cl}(\text{SL})$ | 3 | 0.93746 | -220.82 | -3382.1 | 967.09 | -70 to 80 | 14 |
| 22. | $\text{CHFCl}_2(\text{SL})$ | 3 | 0.77124 | -1174.6 | 14790 | -9977.9 | -65 to 160 | 20 |
| 23. | $\text{CF}_3\text{Cl}(\text{SL})$ | 3 | 0.68190 | -2047.4 | 28685 | -17482 | -140 to 25 | 11 |
| 24. | $\text{CF}_2\text{Cl}_2(\text{SL})$ | 3 | 1.0213 | -232.75 | -1012.0 | -1581.0 | -122 to 110 | 18 |
| 25. | $\text{CFCl}_3(\text{SL})$ | 3 | 0.92841 | -629.42 | 5233.5 | -4814.0 | -40 to 185 | 16 |

TABLE 3: SUMMARY OF REGRESSION ERRORS AND STANDARD DEVIATIONS

| | |
|-------------|--|
| Equation 1: | $d = A + BT + CT^2$ |
| 2: | $d_c = A + BT + CT^2 + DT^3$ |
| 3: | $d - d_c = A(1 - T_r)^{1/3} + B(1 - T_r)^{2/3} + C(1 - T_r) + D(1 - T_r)^{4/3}$ |
| where | d = density, gcm^{-3} ; d_c = critical density, gcm^{-3} (Kudchadker, et.al. (90)) |
| | T = temperature, K ; T_c = critical temperature, K (Kudchadker, et.al. (90)) |
| | T_r = reduced temperature = T/T_c |
| | N = Number of data points used in the final regression |
| | A, B, C, D = regression constants |
| | T_1 = temperature at which regression error is largest, $^{\circ}\text{C}$ |
| | T_2 = temperature at which regression error is smallest, $^{\circ}\text{C}$ |

Note: The numbers in parentheses next to the figures in the maximum error and minimum error columns pertain to the reference from which the regressed value was drawn.

| SL. No. | Compound and State | Eqn. No. | Average error $\times 10^{-3}$ | Maximum error $\times 10^4$ | $T_1, ^{\circ}\text{C}$ | Minimum error $\times 10^4$ | $T_2, ^{\circ}\text{C}$ | Standard deviation $\times 10^1$ |
|---------|-------------------------------------|----------|--------------------------------|-----------------------------|-------------------------|-----------------------------|-------------------------|----------------------------------|
| 1. | $\text{CH}_3\text{F}(\text{SL})$ | 1 | 0.021 | 0.36 (59) | -100.0 | 0.08 (59) | -130.0 | 0.104 |
| 2. | $\text{CH}_2\text{F}_2(\text{L})$ | 2 | 0.190 | 3.0 (99) | -72.87 | 0.40 (99) | -28.4 | 0.652 |
| 3. | $\text{CHF}_3(\text{SL})$ | 3 | 1.63 | 57.2 (74) | 24.02 | 2.85 (3) | -72.3 | 4.90 |
| 4. | $\text{CF}_4(\text{SL})$ | 1 | 0.37 | -13.1 (85) | -93.71 | -0.69 (85) | -140.2 | 1.25 |
| 5. | $\text{CH}_3\text{Cl}(\text{L})$ | 1 | 0.216 | 6.45 (113) | -70.0 | 0.03 (113) | -60.0 | 1.06 |
| 6. | $\text{CH}_3\text{Cl}(\text{SL})$ | 3 | 0.431 | -7.87 (75) | -40.0 | -0.45 (75) | -110.0 | 1.16 |
| 7. | $\text{CH}_2\text{Cl}_2(\text{L})$ | 1 | 0.224 | 7.59 (113) | 28.3 | -0.34 (162) | 0.0 | 0.475 |
| 8. | $\text{CH}_2\text{Cl}_2(\text{SL})$ | 2 | 0.021 | 0.49 (130) | 4.11 | -0.06 (130) | 55.06 | 0.068 |

Table 3 (contd.)

| Sl. No. | Compound and State | Eqn. No. | Average error $\times 10^{-3}$ | Maximum error $\times 10^4$ | $T_1, ^\circ\text{C}$ | Minimum error $\times 10^4$ | $T_2, ^\circ\text{C}$ | Standard deviation $\times 10^4$ |
|---------|-------------------------------------|----------|--------------------------------|-----------------------------|-----------------------|-----------------------------|-----------------------|----------------------------------|
| 9. | $\text{CHCl}_3(\text{L})$ | 1 | 0.138 | -3.15 (159) | -35.3 | 0.11 (159) | 15.0 | 0.419 |
| 10. | $\text{CHCl}_3(\text{SL})$ | 3 | 1.49 | 96.8 (26) | 262.5 | 0.07 (26) | 167.6 | 4.78 |
| 11.a. | $\text{CCl}_4(\text{L})$ | 1 | 0.088 | 1.62 (48) | 17.75 | -0.01 (124) | 40.0 | 0.228 |
| 11.b. | $\text{CCl}_4(\text{L})$ | 1 | 0.047 | -1.90 (164) | 30.0 | -0.01 (124) | 40.0 | 0.193 |
| 12. | $\text{CCl}_4(\text{SL})$ | 3 | 0.618 | -16.1 (194) | 180.0 | -0.07 (87) | 99.8 | 0.861 |
| 13. | $\text{CH}_3\text{Br}(\text{SL})$ | 1 | 1.20 | 25.2 (113) | -57.0 | 1.01 (74) | -50.0 | 3.38 |
| 14. | $\text{CH}_2\text{Br}_2(\text{L})$ | 1 | 0.321 | 8.64 (51) | -74.7 | 0.48 (57) | -15.0 | 1.21 |
| 15. | $\text{nCHBr}_3(\text{L})$ | 1 | 0.408 | -8.99 (148) | 9.96 | 0.52 (148) | 13.93 | 0.835 |
| 16. | $\text{CBr}_4(\text{L})$ | 2 | 1.62 | 34.8 (51) | 100.7 | -6.25 (51) | 124.9 | 6.64 |
| 17. | $\text{CH}_3\text{I}(\text{L})$ | 1 | 0.151 | -5.53 (109) | 25.0 | -0.57 (161) | 0.0 | 0.47 |
| 18. | $\text{CH}_3\text{I}(\text{SL})$ | 2 | 0.230 | 5.38 (113) | -30.0 | 0.81 (113) | 30.0 | 0.785 |
| 19. | $\text{CH}_2\text{I}_2(\text{L})$ | 1 | 0.188 | -5.37 (57) | 40.0 | 0.61 (57) | 120.0 | 0.520 |
| 20. | $\text{CH}_2\text{FCl}(\text{SL})$ | 2 | 0.076 | -2.52 (130) | -47.27 | 0.06 (130) | 11.01 | 0.386 |
| 21. | $\text{CHF}_2\text{Cl}(\text{SL})$ | 3 | 0.448 | -7.95 (130) | -57.74 | -0.52 (13) | 79.77 | 1.35 |
| 22. | $\text{CHFCl}_2(\text{SL})$ | 3 | 0.269 | -7.78 (3) | -65.37 | -0.15 (13) | 15.56 | 0.799 |
| 23. | $\text{CF}_3\text{Cl}(\text{SL})$ | 3 | 1.09 | -25.4 (2) | -61.5 | 1.42 (2) | -142.25 | 4.40 |
| 24. | $\text{CF}_2\text{Cl}_2(\text{SL})$ | 3 | 1.79 | -48.7 (105) | 106.7 | 5.09 (105) | -9.50 | 5.21 |
| 25. | $\text{CFCl}_3(\text{SL})$ | 3 | 0.210 | 5.20 (14) | 170.0 | 0.49 (14) | 0.0 | 0.617 |

TABLE 4: CALCULATED AND EXPERIMENTAL DENSITIES AT SELECTED TEMPERATURES

Note: The reference densities are given below the calculated values. For the reference densities, the pertinent reference is in each case indicated in parentheses

| Sl. No. | Compound and State | Eqn. No. | Density, gm ⁻³ | | |
|---------|--------------------------------------|----------|---------------------------|--------------------------|--------------------------|
| | | | 15°C | 20°C | 25°C |
| 1. | CH ₃ F(SL) | 1 | - | - | - |
| 2. | CH ₂ F ₂ (L) | 2 | 1.0722 | 1.0311 | 0.9897 |
| 3. | CHF ₃ (SL) | 3 | 0.8817 | 0.8079 | 0.6719 (0.67007(73)) |
| 4. | CF ₄ (SL) | 1 | - | - | - |
| 5. | CH ₃ Cl(L) | 1 | - | - | - |
| 6. | CH ₂ Cl(SL) | 3 | 0.9942 | 0.9158 | 0.9071 |
| 7. | CH ₂ Cl ₂ (L) | 1 | 1.3347 (1.33479(162)) | 1.3257 (1.3255(46)) | 1.3167 (1.3169(9)) |
| 8. | CH ₂ Cl ₂ (SL) | 2 | 1.3350 | 1.3255 | 1.3160 |
| 9. | CHCl ₃ (L) | 1 | 1.49850 (1.49845(163)) | 1.48916 (1.4895(113)) | 1.47982 (1.4795(109)) |
| 10. | CHCl ₃ (SL) | 3 | - | - | - |
| 11a. | CCl ₄ (L) | 1 | 1.60380 (1.6037(164)) | 1.59415 (1.59397(41)) | 1.58444 (1.58429(41)) |
| 11b. | CCl ₄ (L) | 1 | 1.60375 (1.6037(164)) | 1.59408 (1.59397(41)) | 1.58436 (1.58429(41)) |
| 12. | CCl ₄ (SL) | 3 | 1.6034 | 1.5938 (1.5939(194)) | 1.5842 (1.58435(23)) |
| | | | | | 1.5746 (1.5748(194)) |

Table 4 (contd)

| Sl. No. | Compound and State | Eqn. No. | Density, g cm ⁻³ | | |
|---------|--------------------------------------|----------|-----------------------------|--------------------------|----------------------------------|
| | | | 15°C | 20°C | 25°C |
| 13. | CH ₃ Br (SL) | 1 | 1.6893 | 1.6758 (1.6769(74)) | 1.6622 1.6485 (1.6489(74)) |
| 14. | CH ₂ Br ₂ (L) | 1 | 2.5099 (2.50986(162)) | 2.4969 (2.4970(148)) | 2.4707 (2.47133(162)) |
| 15. | CHBr ₃ (L) | 1 | 2.9039 (2.90350(163)) | 2.8909 (2.8889(148)) | 2.8648 (2.86460(163)) |
| 16. | CBr ₄ (L) | 2 | - | - | - |
| 17. | CH ₃ I(L) | 1 | 2.29316 (2.33504(161)) | 2.27913 (2.2790(185)) | 2.26505 (2.2645(109)) |
| 18. | CH ₃ I(SL) | 2 | 2.2864 | 2.2720 (2.272(113)) | 2.2575 2.2067 (2.243(113)) |
| 19. | CH ₂ I ₂ (L) | 1 | 3.3344 (3.3345(160)) | 3.3211 (3.3212(160)) | 3.2947 (3.2944(160)) |
| 20. | CH ₂ FCI(SL) | 2 | 1.2104 | 1.1970 | 1.1834 1.1696 |
| 21. | CHF ₂ Cl(SL) | 3 | 1.2322 | 1.2134 | 1.1940 1.1739 |
| 22. | CHFCl ₂ (SL) | 3 | 1.3904 | 1.3784 | 1.3663 1.3540 |
| 23. | CF ₃ Cl(SL) | 3 | 0.9808 | 0.9139 | 0.8170 - |
| 24. | CF ₂ Cl ₂ (SL) | 3 | 1.3451 | 1.3275 (1.3290(15)) | 1.3095 1.2910 (1.2930(15)) |
| 25. | CFCl ₃ (SL) | 3 | 1.4996 | 1.4879 | 1.4760 1.4640 |

TABLE 5: CALCULATED AND EXPERIMENTAL DENSITIES AT THE HIGHEST AND LOWEST REGRESSION TEMPERATURES

Note: The reference densities are given below the calculated values.
 For the reference densities, the pertinent reference is in each case indicated in parentheses
 T_H = highest regressed temperature, °C ; T_L = lowest regressed temperature, °C

| Sl. No. | Compound and State | Eqn. No. | T_H , °C | T_L , °C | Density, gcm^{-3} | |
|---------|-------------------------------|----------|------------|------------|----------------------------|---------------------------|
| | | | | | T_H , °C | T_L , °C |
| 1. | CH_3F (SL) | 1 | -60.0 | -130.0 | 0.8423 (0.8428(59)) | 0.9827 (0.9827(59)) |
| 2. | CH_2F_2 (L) | 2 | 14.16 | -72.87 | 1.0790 (1.0793(99)) | 1.7631 (1.7628(99)) |
| 3. | CHF_3 (SL) | 3 | 25.52 | -83.12 | 0.6360 (0.6370(74)) | 1.4445 (1.4432(74)) |
| 4. | CF_4 (SL) | 1 | -114.74 | -180.75 | 1.542 (1.542(1)) | 1.872 (1.872(1)) |
| 5. | CH_3Cl (L) | 1 | -20.0 | -90.0 | 1.005 (1.005 (113)) | 1.119 (1.119(113)) |
| 6. | CH_3Cl (SL) | 3 | 130.0 | 20.0 | 0.5895 (0.5889(75)) | 0.9158 (0.9159(148)) |
| 7. | CH_2Cl_2 (L) | 1 | 30.0 | -100.0 | 1.3077 (1.30777(162)) | 1.5393 (1.539(113)) |
| 8. | CH_2Cl_2 (SL) | 2 | 100.78 | -64.77 | 1.1658 (1.1659(130)) | 1.4793 (1.4792(130)) |
| 9. | CHCl_3 (L) | 1 | 30.0 | -63.90 | 1.47046 (1.47060 (163)) | 1.64337 (1.64312(159)) |
| 10. | CHCl_3 (SL) | 3 | 262.8 | -101.4 | 0.5657 (0.5662 (261)) | 1.4910 |

Table 5 (Contd.)

| Sl. No. | Compound and State | Eqn. No. | $T_H, ^\circ\text{C}$ | $T_L, ^\circ\text{C}$ | Density, gcm^{-3} | |
|---------|------------------------------------|----------|-----------------------|-----------------------|----------------------------|---------------------------|
| | | | | | $T_H, ^\circ\text{C}$ | $T_L, ^\circ\text{C}$ |
| 11a. | $\text{CCl}_4(\text{L})$ | 1 | 70.0 | 0.0 | 1.49438 (1.49454 (151)) | 1.63241 (1.63255(167)) |
| 11b. | $\text{CCl}_4(\text{L})$ | 1. | 40.0 | 0.0 | 1.55498 (1.55498(124)) | 1.63252 (1.63255(167)) |
| 12. | $\text{CCl}_4(\text{SL})$ | 3 | 264.15 | 19.5 | 0.9118 (0.9120(27)) | 1.5948 (1.5946(131)) |
| 13. | $\text{CH}_3\text{Br}(\text{SL})$ | 1 | 50.0 | -93.6 | 1.5928 (1.5910 (74)) | 1.9618 (1.9640(113)) |
| 14. | $\text{CH}_2\text{Br}_2(\text{L})$ | 1 | 97.2 | 0.0 | 2.2898 (2.2905(51)) | 2.54874 (2.54852(162)) |
| 15. | $\text{CHBr}_3(\text{L})$ | 1 | 123.4 | 9.32 | 2.6105 (2.6113(51)) | 2.9186 (2.9187(158)) |
| 16. | $\text{CBr}_4(\text{L})$ | 2 | 190.0 | 100.0 | 2.6963 (2.6970(51)) | 2.9582 (2.9609(174)) |
| 17. | $\text{CH}_3\text{I}(\text{L})$ | 1 | 30.0 | 0.0 | 2.25093 (2.25102 (161)) | 2.33498 (2.33504(161)) |
| 18. | $\text{CH}_3\text{I}(\text{SL})$ | 2 | 40.0 | -70.0 | 2.2141 (2.214 (113)) | 2.5298 (2.530(113)) |
| 19. | $\text{CH}_2\text{I}_2(\text{L})$ | 1 | 120.0 | 15.0 | 3.0707 (3.0708 (57)) | 3.3344 (3.3345(160)) |
| 20. | $\text{CH}_2\text{FCl}(\text{SL})$ | 2 | 41.4 | -80.95 | 1.1382 (1.1374(130)) | 1.4456 (1.4462(130)) |
| 21. | $\text{CHF}_2\text{Cl}(\text{SL})$ | 3 | 79.77 | -67.78 | 0.8967 (0.8968 (13)) | 1.4858 (1.4852(13)) |

Table 5 (Contd.)

| Sl. No. | Compound and State | Eqn. No. | $T_H, ^\circ C$ | $T_L, ^\circ C$ | Density, gm^{-3} | |
|---------|--------------------|----------|-----------------|-----------------|-------------------------|-------------------------|
| | | | | | $T_H, ^\circ C$ | $T_L, ^\circ C$ |
| 22. | $CHFCl_2$ (SL) | 3 | 157.9 | -65.37 | 0.8963 (0.8965(13)) | 1.5690 (1.5698(3)) |
| 23. | CF_3Cl (SL) | 3 | 25.044 | -142.25 | 0.8158 (0.8153(2)) | 1.7378 (1.7377(2)) |
| 24. | CF_2Cl_2 (SL) | 3 | 106.7 | -121.9 | 0.8091 (0.8140(105)) | 1.7321 (1.7341(105)) |
| 25. | $CFCl_3$ (SL) | 3 | 183.4 | -40.0 | 0.8968 (0.8965 (13)) | 1.6219 (1.6218(13)) |

TABLE 6 : CALCULATED DENSITIES FOR FLUOROMETHANES

| Temperature, °C | Density, g cm ⁻³ | | | |
|--------------------|-----------------------------|------------------------------------|----------------------|---------------------|
| | CH ₃ F(SL) | CH ₂ F ₂ (L) | CHF ₃ (L) | CF ₄ (L) |
| -180 | | | | 1.868 |
| -175 | | | | 1.845 |
| -170 | | | | 1.821 |
| -165 | | | | 1.797 |
| -160 | | | | 1.773 |
| -155 | | | | 1.749 |
| -150 | | | | 1.724 |
| -145 | | | | 1.699 |
| -140 | | | | 1.674 |
| -135 | | | | 1.648 |
| -130 | 0.9827 | | | 1.623 |
| -125 | 0.9733 | | | 1.597 |
| -120 | 0.9639 | | | 1.570 |
| -115 | 0.9544 | | | 1.544 |
| -110 | 0.9447 | | | 1.517 |
| -105 | 0.9350 | | | |
| -100 | 0.9251 | | | |
| - 95 | 0.9152 | | | |
| - 90 | 0.9052 | | | |
| - 85 | 0.8950 | | 1.4501 | |
| - 80 | 0.8848 | | 1.4332 | |
| - 75 | 0.8744 | 1.7796 | 1.4156 | |
| - 70 | 0.8640 | 1.7409 | 1.3974 | |
| - 65 | 0.8535 | 1.7023 | 1.3785 | |
| - 60 | 0.8428 | 1.6637 | 1.3588 | |
| - 55 | | 1.6250 | 1.3383 | |
| - 50 | | 1.5863 | 1.3170 | |
| - 45 | | 1.5476 | 1.2947 | |
| - 40 | | 1.5088 | 1.2714 | |

contd....2

Table 6 (contd.)

| Temperature, °C | Density, g cm ⁻³ | | | |
|--------------------|-----------------------------|------------------------------------|----------------------|---------------------|
| | CH ₃ F(SL) | CH ₂ F ₂ (L) | CHF ₃ (L) | CF ₄ (L) |
| - 35 | | 1.4699 | 1.2469 | |
| - 30 | | 1.4309 | 1.2212 | |
| - 25 | | 1.3918 | 1.1942 | |
| - 20 | | 1.3526 | 1.1655 | |
| - 15 | | 1.3131 | 1.1351 | |
| - 10 | | 1.2735 | 1.1025 | |
| - 5 | | 1.2337 | 1.0674 | |
| 0 | | 1.1937 | 1.0292 | |
| 5 | | 1.1535 | 0.9868 | |
| 10 | | 1.1130 | 0.9387 | |
| 15 | | 1.0722 | 0.8817 | |
| 20 | | | 0.8079 | |
| 25 | | | 0.6719 | |

TABLE 7A: CALCULATED DENSITIES FOR CHLOROMETHANES

| t, °C | Density, gcm^{-3} | | | |
|-------|----------------------------------|-----------------------------------|------------------------------------|-------------------------------------|
| | $\text{CH}_3\text{Cl}(\text{L})$ | $\text{CH}_3\text{Cl}(\text{SL})$ | $\text{CH}_2\text{Cl}_2(\text{L})$ | $\text{CH}_2\text{Cl}_2(\text{SL})$ |
| -100 | | | 1.5393 | |
| - 95 | | | 1.5305 | |
| - 90 | 1.119 | | 1.5217 | |
| - 85 | 1.110 | | 1.5129 | |
| - 80 | 1.102 | | 1.5041 | |
| - 75 | 1.093 | | 1.4952 | |
| - 70 | 1.085 | | 1.4864 | |
| - 65 | 1.076 | | 1.4776 | 1.4796 |
| - 60 | 1.068 | | 1.4687 | 1.4709 |
| - 55 | 1.060 | | 1.4598 | 1.4622 |
| - 50 | 1.052 | | 1.4510 | 1.4535 |
| - 45 | 1.044 | | 1.4421 | 1.4447 |
| - 40 | 1.036 | | 1.4332 | 1.4358 |
| - 35 | 1.028 | | 1.4243 | 1.4269 |
| - 30 | 1.020 | | 1.4154 | 1.4180 |
| - 25 | 1.013 | | 1.4065 | 1.4090 |
| - 20 | | | 1.3975 | 1.3999 |
| - 15 | | | 1.3886 | 1.3908 |
| - 10 | | | 1.3796 | 1.3816 |
| - 5 | | | 1.3707 | 1.3724 |
| 0 | | | 1.3617 | 1.3631 |
| 5 | | | 1.3527 | 1.3537 |
| 10 | | | 1.3437 | 1.3444 |
| 15 | | | 1.3347 | 1.3349 |
| 20 | | | 1.3257 | 1.3255 |
| 25 | | | 1.3167 | 1.3159 |
| 30 | | | 1.3077 | 1.3063 |
| 35 | | 0.8886 | 1.2986 | 1.2967 |
| 40 | | 0.8788 | 1.2896 | 1.2870 |
| 45 | | 0.8687 | | 1.2773 |
| 50 | | 0.8581 | | 1.2676 |

TABLE 7A(Contd.)

| t, °C | Density, gcm ⁻³ | | | |
|-------|----------------------------|------------------------|-------------------------------------|--------------------------------------|
| | CH ₃ Cl(L) | CH ₃ Cl(SL) | CH ₂ Cl ₂ (L) | CH ₂ Cl ₂ (SL) |
| 55 | | 0.8471 | | 1.2577 |
| 60 | | 0.8357 | | 1.2479 |
| 65 | | 0.8238 | | 1.2380 |
| 70 | | 0.8114 | | 1.2280 |
| 75 | | 0.7984 | | 1.2180 |
| 80 | | 0.7848 | | 1.2080 |
| 85 | | 0.7706 | | 1.1979 |
| 90 | | 0.7557 | | 1.1878 |
| 95 | | 0.7399 | | 1.1776 |
| 100 | | 0.7233 | | 1.1674 |
| 105 | | 0.7055 | | |
| 110 | | 0.6866 | | |
| 115 | | 0.6660 | | |
| 120 | | 0.6436 | | |
| 125 | | 0.6185 | | |
| 130 | | 0.5895 | | |
| 135 | | 0.5539 | | |

TABLE 7B : CALCULATED DENSITIES FOR CHLOROMETHANES

| t, °C | Density, gcm ⁻³ | | | | |
|-------|----------------------------|------------------------|----------------------|----------------------|-----------------------|
| | CHCl ₃ (L) | CHCl ₃ (SL) | CCl ₄ (L) | CCl ₄ (L) | CCl ₄ (SL) |
| - 65 | 1.64648 | | | | |
| - 60 | 1.63731 | | | | |
| - 55 | 1.62813 | | | | |
| - 50 | 1.61894 | | | | |
| - 45 | 1.60973 | | | | |
| - 40 | 1.60052 | | | | |
| - 35 | 1.59130 | | | | |
| - 30 | 1.58206 | | | | |
| - 25 | 1.57282 | | | | |
| - 20 | 1.56757 | | | | |
| - 15 | 1.55430 | | | | |
| - 10 | 1.54503 | | | | |
| - 5 | 1.53574 | | | | |
| - 0 | 1.52645 | | 1.66982 | 1.63241 | |
| 5 | 1.51714 | | 1.66165 | 1.62293 | |
| 10 | 1.50782 | | 1.65346 | 1.61340 | |
| 15 | 1.49850 | | 1.64526 | 1.60380 | |
| 20 | 1.48916 | | 1.63704 | 1.59415 | 1.5938 |
| 25 | 1.47981 | | 1.62880 | 1.58444 | 1.5843 |
| 30 | 1.47046 | | 1.62055 | 1.57467 | 1.5746 |
| 35 | | | 1.61229 | 1.56484 | 1.5649 |
| 40 | | | 1.60400 | 1.55495 | 1.5552 |
| 45 | | | | 1.54500 | 1.5455 |
| 50 | | | | 1.53500 | 1.5356 |
| 55 | | | | 1.52493 | 1.5258 |
| 60 | | | | 1.51481 | 1.5159 |
| 65 | | | | 1.50462 | 1.5059 |
| 70 | | | | 1.49438 | 1.4958 |

TABLE 7B (Contd.)

| t, °C | Density, gcm ⁻³ | | | | |
|-------|----------------------------|------------------------|----------------------|----------------------|-----------------------|
| | CHCl ₃ (L) | CHCl ₃ (SL) | CCl ₄ (L) | CCl ₄ (L) | CCl ₄ (SL) |
| 75 | | | | | 1.4857 |
| 80 | | | | | 1.4755 |
| 85 | | | | | 1.4652 |
| 90 | | | | | 1.4549 |
| 95 | | | | | 1.4444 |
| 100 | | | | | 1.4339 |
| 105 | | | | | 1.4232 |
| 110 | | 1.4580 | | | 1.4125 |
| 115 | | 1.4389 | | | 1.4016 |
| 120 | | 1.4197 | | | 1.3906 |
| 125 | | 1.4005 | | | 1.3795 |
| 130 | | 1.3813 | | | 1.3683 |
| 135 | | 1.3621 | | | 1.3569 |
| 140 | | 1.3428 | | | 1.3453 |
| 145 | | 1.3235 | | | 1.3336 |
| 150 | | 1.3040 | | | 1.3217 |
| 155 | | 1.2845 | | | 1.3096 |
| 160 | | 1.2648 | | | 1.2973 |
| 165 | | 1.2450 | | | 1.2847 |
| 170 | | 1.2250 | | | 1.2719 |
| 175 | | 1.2048 | | | 1.2588 |
| 180 | | 1.1843 | | | 1.2454 |
| 185 | | 1.1635 | | | 1.2317 |
| 190 | | 1.1424 | | | 1.2176 |
| 195 | | 1.1209 | | | 1.2031 |
| 200 | | 1.0989 | | | 1.1882 |
| 205 | | 1.0762 | | | 1.1728 |
| 210 | | 1.0529 | | | 1.1569 |
| 215 | | 1.0287 | | | 1.1403 |
| 220 | | 1.0035 | | | 1.1231 |
| 225 | | 0.9769 | | | 1.1050 |
| 230 | | 0.9487 | | | 1.0861 |
| 235 | | 0.9184 | | | 1.0660 |

TABLE 7B: (contd.)

| t, °C | Density, gcm ⁻³ | | | | |
|-------|----------------------------|------------------------|----------------------|----------------------|-----------------------|
| | CHCl ₃ (L) | CHCl ₃ (SL) | CCl ₄ (L) | CCl ₄ (L) | CCl ₄ (SL) |
| 240 | | 0.8852 | | | 1.0448 |
| 245 | | 0.8479 | | | 1.0219 |
| 250 | | 0.8044 | | | 0.9973 |
| 255 | | 0.7501 | | | 0.9702 |
| 260 | | | | | 0.9401 |
| 265 | | | | | 0.9056 |
| 270 | | | | | 0.8647 |
| 275 | | | | | 0.8128 |
| 280 | | | | | 0.7345 |

TABLE 8 : CALCULATED DENSITIES FOR BROMOMETHANES

| Temperature, °C | Density, gcm ⁻³ | | | |
|--------------------|----------------------------|-------------------------------------|-----------------------|----------------------|
| | CH ₃ Br(SL) | CH ₂ Br ₂ (L) | CHBr ₃ (L) | CBr ₄ (L) |
| -95 | 1.965 | | | |
| -90 | 1.953 | | | |
| -85 | 1.942 | | | |
| -80 | 1.930 | | | |
| -75 | 1.918 | | | |
| -70 | 1.906 | | | |
| -65 | 1.894 | | | |
| -60 | 1.882 | | | |
| -65 | 1.870 | | | |
| -50 | 1.857 | | | |
| -45 | 1.845 | | | |
| -40 | 1.832 | | | |
| -35 | 1.820 | | | |
| -30 | 1.807 | | | |
| -25 | 1.794 | | | |
| -20 | 1.782 | | | |
| -15 | 1.769 | | | |
| -10 | 1.756 | | | |
| - 5 | 1.743 | | | |
| 0 | 1.729 | 2.5488 | | |
| 5 | 1.716 | 2.5359 | | |
| 10 | 1.703 | 2.5229 | 2.9168 | |
| 15 | 1.689 | 2.5099 | 2.9039 | |
| 20 | | 2.4969 | 2.8909 | |
| 25 | | 2.4838 | 2.8779 | |
| 30 | | 2.4707 | 2.8648 | |
| 35 | | 2.4575 | 2.8517 | |
| 40 | | 2.4443 | 2.8385 | |
| 45 | | 2.4310 | 2.8252 | |
| 50 | | 2.4177 | 2.8119 | |

Table 8 (contd.)

| Temperature, °C | Density, gcm ⁻³ | | | |
|--------------------|----------------------------|-------------------------------------|-----------------------|----------------------|
| | CH ₃ Br(SL) | CH ₂ Br ₂ (L) | CHBr ₃ (L) | CBr ₄ (L) |
| 55 | | 2.4044 | 2.7986 | |
| 60 | | 2.3909 | 2.7852 | |
| 65 | | 2.3775 | 2.7717 | |
| 70 | | 2.3640 | 2.7582 | |
| 75 | | 2.3505 | 2.7446 | |
| 80 | | 2.3369 | 2.7310 | |
| 85 | | 2.3232 | 2.7173 | |
| 90 | | 2.3096 | 2.7036 | |
| 95 | | 2.2959 | 2.6898 | |
| 100 | | 2.2821 | 2.6760 | 2.9582 |
| 105 | | | 2.6621 | 2.9479 |
| 110 | | | 2.6481 | 2.9368 |
| 115 | | | 2.6341 | 2.9250 |
| 120 | | | 2.6201 | 2.9126 |
| 125 | | | 2.6060 | 2.8995 |
| 130 | | | | 2.8859 |
| 135 | | | | 2.8718 |
| 140 | | | | 2.8572 |
| 145 | | | | 2.8421 |
| 150 | | | | 2.8268 |
| 155 | | | | 2.8111 |
| 160 | | | | 2.7951 |
| 165 | | | | 2.7789 |
| 170 | | | | 2.7625 |
| 175 | | | | 2.7460 |
| 180 | | | | 2.7294 |
| 185 | | | | 2.7128 |
| 190 | | | | 2.6963 |

TABLE 9 : CALCULATED DENSITIES FOR IODOMETHANES

| Temperature, °C | Density, gcm ⁻³ | | |
|--------------------|----------------------------|-----------------------|------------------------------------|
| | CH ₃ I(L) | CH ₃ I(SL) | CH ₂ I ₂ (L) |
| -70 | | 2.543 | |
| -65 | | 2.530 | |
| -60 | | 2.516 | |
| -55 | | 2.503 | |
| -50 | | 2.490 | |
| -45 | | 2.477 | |
| -40 | | 2.464 | |
| -35 | | 2.451 | |
| -30 | | 2.438 | |
| -25 | | 2.425 | |
| -20 | | 2.412 | |
| -15 | | 2.399 | |
| -10 | | 2.387 | |
| - 5 | | 2.374 | |
| 0 | 2.3350 | 2.361 | |
| 5 | 2.3211 | 2.349 | |
| 10 | 2.3072 | 2.336 | |
| 15 | 2.2932 | 2.324 | 3.3344 |
| 20 | 2.2791 | 2.311 | 3.3211 |
| 25 | 2.2651 | 2.299 | 3.3078 |
| 30 | 2.2509 | 2.286 | 3.2947 |
| 35 | | 2.274 | 3.2816 |
| 40 | | 2.262 | 3.2686 |
| 45 | | | 3.2556 |
| 50 | | | 3.2428 |
| 55 | | | 3.2300 |
| 60 | | | 3.2173 |
| 65 | | | 3.2046 |
| 70 | | | 3.1921 |
| 75 | | | 3.1796 |

Table 9 (continued)

| Temperature, °C | Density, gcm ⁻³ | | |
|--------------------|----------------------------|-----------------------|------------------------------------|
| | CH ₃ I(L) | CH ₃ I(SL) | CH ₂ I ₂ (L) |
| 80 | | | 3.1672 |
| 85 | | | 3.1549 |
| 90 | | | 3.1426 |
| 95 | | | 3.1304 |
| 100 | | | 3.1184 |
| 105 | | | 3.1063 |
| 110 | | | 3.0944 |
| 115 | | | 3.0825 |
| 120 | | | 3.0707 |

TABLE 10: CALCULATED DENSITIES FOR THE MIXED HALOMETHANES

| t, °C | Density, gcm ⁻³ | | | | | |
|-------|----------------------------|-------------------------|-------------------------|------------------------|--------------------------------------|------------------------|
| | CH ₂ FCI(SL) | CHF ₂ Cl(SL) | CHFCI ₂ (SL) | CF ₃ Cl(SL) | CF ₂ Cl ₂ (SL) | CFCl ₃ (SL) |
| -140 | | | | 1.7301 | | |
| -135 | | | | 1.7128 | | |
| -130 | | | | 1.6954 | | |
| -125 | | | | 1.6779 | | |
| -120 | | | | 1.6603 | 1.7274 | |
| -115 | | | | 1.6426 | 1.7152 | |
| -110 | | | | 1.6248 | 1.7028 | |
| -105 | | | | 1.6068 | 1.6903 | |
| -100 | | | | 1.5887 | 1.6778 | |
| - 95 | | | | 1.5704 | 1.6651 | |
| - 90 | | | | 1.5519 | 1.6523 | |
| - 85 | | | | 1.5331 | 1.6394 | |
| - 80 | 1.4441 | | | 1.5141 | 1.6264 | |
| - 75 | 1.4323 | | | 1.4948 | 1.6133 | |
| - 70 | 1.4204 | 1.4916 | | 1.4751 | 1.6000 | |
| - 65 | 1.4086 | 1.4784 | 1.5682 | 1.4551 | 1.5866 | |
| - 60 | 1.3968 | 1.4651 | 1.5577 | 1.4347 | 1.5730 | |
| - 55 | 1.3849 | 1.4516 | 1.5470 | 1.4138 | 1.5593 | |
| - 50 | 1.3730 | 1.4378 | 1.5363 | 1.3923 | 1.5455 | |
| - 45 | 1.3611 | 1.4238 | 1.5256 | 1.3703 | 1.5314 | |
| - 40 | 1.3491 | 1.4096 | 1.5147 | 1.3475 | 1.5172 | 1.6223 |
| - 35 | 1.3371 | 1.3951 | 1.5039 | 1.3239 | 1.5028 | 1.6116 |
| - 30 | 1.3250 | 1.3804 | 1.4929 | 1.2994 | 1.4882 | 1.6009 |
| - 25 | 1.3128 | 1.3653 | 1.4819 | 1.2737 | 1.4734 | 1.5901 |
| - 20 | 1.3005 | 1.3500 | 1.4708 | 1.2468 | 1.4583 | 1.5792 |
| - 15 | 1.2882 | 1.3344 | 1.4596 | 1.2182 | 1.4430 | 1.5682 |
| - 10 | 1.2757 | 1.3184 | 1.4483 | 1.1878 | 1.4275 | 1.5571 |
| - 5 | 1.2631 | 1.3020 | 1.4369 | 1.1550 | 1.4116 | 1.5459 |
| - 0 | 1.2503 | 1.2852 | 1.4254 | 1.1192 | 1.3955 | 1.5346 |
| 5 | 1.2374 | 1.2680 | 1.4138 | 1.0794 | 1.3791 | 1.5232 |
| 10 | 1.2244 | 1.2504 | 1.4021 | 1.0342 | 1.3623 | 1.5117 |
| 15 | 1.2112 | 1.2322 | 1.3903 | 0.9809 | 1.3451 | 1.5001 |

TABLE 10(Contd.)

| t, °C | Density, gcm ⁻³ | | | | | |
|-------|----------------------------|-------------------------|-------------------------|------------------------|--------------------------------------|------------------------|
| | CH ₂ FCI(SL) | CHF ₂ Cl(SL) | CHFCl ₂ (SL) | CF ₃ Cl(SL) | CF ₂ Cl ₂ (SL) | CFCI ₃ (SL) |
| 20 | 1.1978 | 1.2134 | 1.3784 | 0.9139 | 1.3275 | 1.4884 |
| 25 | 1.1843 | 1.1940 | 1.3663 | 0.8170 | 1.3095 | 1.4765 |
| 30 | 1.1705 | 1.1739 | 1.3540 | | 1.2910 | 1.4645 |
| 35 | 1.1566 | 1.1530 | 1.3416 | | 1.2719 | 1.4524 |
| 40 | 1.1424 | 1.1313 | 1.3290 | | 1.2523 | 1.4401 |
| 45 | | 1.1085 | 1.3163 | | 1.2319 | 1.4276 |
| 50 | | 1.0845 | 1.3033 | | 1.2108 | 1.4150 |
| 55 | | 1.0590 | 1.2901 | | 1.1888 | 1.4022 |
| 60 | | 1.0319 | 1.2767 | | 1.1658 | 1.3892 |
| 65 | | 1.0027 | 1.2630 | | 1.1416 | 1.3760 |
| 70 | | 0.9708 | 1.2491 | | 1.1160 | 1.3625 |
| 75 | | 0.9353 | 1.2348 | | 1.0887 | 1.3489 |
| 80 | | 0.8947 | 1.2202 | | 1.0593 | 1.3350 |
| 85 | | | 1.2053 | | 1.0272 | 1.3208 |
| 90 | | | 1.1900 | | 0.9916 | 1.3063 |
| 95 | | | 1.1742 | | 0.9508 | 1.2915 |
| 100 | | | 1.1580 | | 0.9019 | 1.2764 |
| 105 | | | 1.1412 | | 0.8378 | 1.2609 |
| 110 | | | 1.1237 | | | 1.2449 |
| 115 | | | 1.1056 | | | 1.2286 |
| 120 | | | 1.0867 | | | 1.2117 |
| 125 | | | 1.0669 | | | 1.1942 |
| 130 | | | 1.0461 | | | 1.1762 |
| 135 | | | 1.0239 | | | 1.1574 |
| 140 | | | 1.0003 | | | 1.1379 |
| 145 | | | 0.9748 | | | 1.1174 |
| 150 | | | 0.9470 | | | 1.0959 |
| 155 | | | 0.9161 | | | 1.0731 |
| 160 | | | 0.8809 | | | 1.0488 |
| 165 | | | | | | 1.0227 |
| 170 | | | | | | 0.9942 |
| 175 | | | | | | 0.9627 |
| 180 | | | | | | 0.9269 |
| 185 | | | | | | 0.8848 |